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SOTRAS report 4

METRAS: A one-dimensional model for assessment of leaching of trace metals from soil. Model description and results of a case study for Cd in 'De Kempen'.

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PREFACE

In 1993, the Laboratory for Soil and Groundwater Research of the Dutch National Institute of Public Health and Environmental Protection (RIVM/LBG) started the project 'Standardization of models for Soil and Groundwater' (RIVM project 715501). Aim of this project was to develop a series of standardized models for the assessment of leaching of non-point source pollutants from the soil. These models have primarily been developed for the generation of environmental outlooks (v.d Brink & v.d. Berg, 1995). Model development has been efficient because existing modules were used where possible (e.g. soil water transport and solute transport.

This report presents a model for assessing accumulation and transport of heavy metals from the soil (METRAS). In 1994 a working group started to guide the development of METRAS. This working group consisted of Leo Boumans, Frank Swartjes and the authors of this report. The authors wish to thank the other participants for their contribution to this project. Sandra Boekhold provided the experimental data for verification of the model.

Other models for behaviour of substances in soil that have been developed or adapted within the framework of the Standardization project are:

- a model for soil water transport, SWIF (Tiktak & Bouten, 1992; Tiktak *et al.*, 1994b),
- a model for assessing leaching of pesticides from the soil (Tiktak *et al.*, 1994b), and
- a model for assessing leaching of volatile organic contaminants in the soil (Freijer *et al.*, 1995).

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ABSTRACT

For evaluation of the Dutch environmental policy there is a need for a general model to estimate the accumulation and transport of trace metals in the soil and uppermost groundwater. For this reason, the Metal Transport Assessment (METRAS) model has been developed, which has the following properties:

- modular set-up to facilitate model development and maintenance. The model shares many modules with other models developed at LBG;
- dynamic and process oriented making the model suitable as a tool for scenario analysis both at the local scale, and the regional scale;
- multi-layer, as single-layer models cannot predict breakthrough of pollutants;
- simplified description of the soil chemical system. Application of the model is limited to non-point source pollutants;
- all parameters can be derived from either standard soil surveys using pedo-transfer functions, or can be derived from standard experiments.

This report describes the model implementation for cadmium. It summarizes the theoretical background for the model, the development and structure of the computer program, the verification of the model using batch and column experiments, and it gives guidelines for model use. Moreover, an application of the model to a forest site in 'De Kempen' is described. Although this application of METRAS can by no means be considered a validation study, the application has improved the confidence in the model concept, and has improved our understanding of the behaviour of cadmium in the soil system. Although there is a need for further model validation, and comparison of model results with those of other models, it was concluded that the model currently is a useful tool to predict metal accumulation and leaching, both on a local scale and on a national scale. This particular model application also showed that the problem of leaching of heavy metals to the groundwater may become more serious in the coming decades, in spite of reduced soil loading.

Key words
heavy metals; cadmium; non-point source pollution; leaching; modelling; unsaturated zone; simulation; soil; Kempen.

SAMENVATTING

Ten behoeve van beleidsondersteuning in het kader van de Milieu-Verkenningen is het model METRAS ontwikkeld. Dit model beschrijft het transport en de accumulatie van zware metalen in de bodem en het bovenste grondwater. Het model heeft de volgende eigenschappen:

- modulaire opbouw, waardoor ontwikkeling en onderhoud van het model eenvoudig is. Het model deelt een aantal modules met andere LBG modellen;
- het model is dynamisch en proces-georiënteerd. Hierdoor kan het model zowel in lokale als regionale studies voor scenario-analyses gebruikt worden;
- het model is een meer-lagen model. Dit is nodig, omdat numerieke één-laag modellen niet geschikt zijn voor de berekening van uitspoeling naar het grondwater;
- het model beschrijft een beperkt aantal bodemchemische interacties. Hierdoor wordt het model sneller, maar is vooral geschikt tot diffuse belastingen van zware metalen;
- alle model parameters kunnen worden afgeleid uit standaardgegevens m.b.v. vertaalfuncties, of kunnen direct worden afgeleid uit laboratorium experimenten.

Dit rapport beschrijft de versie van het model voor cadmium. Het beschrijft de theorie en achtergronden, de ontwikkeling en structuur van het computerprogramma, de verificatie van het model aan de hand van schud- en kolomexperimenten en het gebruik van het model. Verder wordt een toepassing van het model in de Kempen beschreven. Hoewel deze toepassing géén validatiestudie was, is het vertrouwen in het modelconcept door deze toepassing toegenomen. Er werd geconcludeerd dat het model geschikt is voor scenario-analyse op zowel een lokale schaal als op een landelijke schaal. Verdere validatie van het model, vergelijking van de resultaten van het model met andere modellen en een analyse van het effect van variaties van o.a. het weer, zijn noodzakelijk. De toepassing van het model in de Kempen heeft aangetoond dat uitspoeling van zware metalen naar het grondwater een probleem is dat in de komende jaren groter wordt.

Trefwoorden

zware metalen; cadmium; diffuse verontreiningen; uitspoeling; modellering; onverzadigde zone; simulatie; bodem; Kempen.

1 INTRODUCTION

Heavy metals and trace metals potentially introduce a risk to human health and to the ecosystem. For this purpose quality standards are used for soil and groundwater. Cd, Cr, Cu, Hg, Ni, Pb and Zn have received most attention with regard to accumulation in soils, uptake by plants and contamination of groundwater. Table 1 gives some common soil, groundwater and crop quality standards which are used for trace metals in the Netherlands.

TABLE 1
Groundwater and crop quality standard with respect to trace metals in the Netherlands.

Metal	Soil		Groundwater		Crops	
	target value[1]	clean up criterion[1]	target value[1]	clean up criterion[1]	cucumber[2]	potatoes[2]
	(mg kg^{-1})		(μg L^{-1})		(mg kg^{-1})	
Cd	0.8	12	0.4	0.6	0.03	0.10
Cr	100	380	1	30		
Cu	36	190	15	75	20	3
Hg	0.3	10	0.05	0.3	0.03	0.02
Ni	35	210	15	75		
Pb	85	530	15	75	0.3	0.2
Zn	140	720	65	800		

[1] Circular interventiewaarden bodemsanering, WBB, 1994

[2] Warenwet, 1988

Heavy metals can enter the soil by atmospheric deposition, as a constituent of fertilizer or manure, as a constituent of pesticides, or as a constituent of waste products. By result the total soil loading will depend on land use. Heavy metals can occur in various forms in the soil: (i) on ion exchange (sorption) sites, (ii) in or on crystalline or non-crystalline precipitates, (iii) incorporated into organic compounds, or (iv) in the soil solution (Dowdy and Volk, 1983). Trace metals are transported in the soil and can thus be leached into the saturated groundwater by convection with the water flux, by hydrodynamic dispersion or by molecular diffusion. Metals are transported as free ions, as chelates or as colloids. Metals are also redistributed after application to the soil by tillage, biological mixing and plant uptake. The fate of a metal after application to the soil depends on the nature of the metal, the type of land use, and on prevailing soil conditions. The most relevant soil conditions are pH, redox potential, organic matter content, clay content and the presence of anionic ligands.

To predict the fate of a metal and to evaluate the effect of reduced soil loadings, changed land-use and soil treatments, simulation models are helpful. These models should describe reactions and transport of metals in the soil taking into account the effects of soil type, land use and climate. Various models have become available to assess the fate of trace metals, but in general these models emphasize the description of metal reactions, in particular equilibrium reactions; eg. MINEQL (Westall *et al.*, 1976), MINEQL+ (Schecher and McAvoy, 1991), EQ3NR (Wolery, 1983), PHREEQE (Parkhurst *et al.*, 1980), and GEOCHEM (Sposito and Mattigod, 1979). Recently also models that allow for transport assessment were introduced (CHARON; De Rooy, 1991; ECOSAT: Keizer and Van Riemsdijk, 1994; PHREEQM: Appelo and Postma, 1993). These models are applicable to a wide range of problems regarding ionic strength, temperature, CO_2 pressure, pH and exotic ligands. However, in general, these models are not practical for regional analyses of trace metal pollution by non-point sources in water-unsaturated soils under a variety of land use forms. These applications are often characterized by a relatively small range of environmental conditions and a limited number of relevant ligands occurring at low concentration. For such applications it was expected that trace metal behaviour could be assessed by taking into account only a small number of reactions and using fairly conventional transport concepts. This expectation, in combination with the need for a standard tool to assess transport and accumulations of chemicals for non point sources has led to the development of the SOTRAS/SiShell (SOil TRansport ASsessment/Simulation Shell) model system (Tiktak *et al.*, 1994a). The main characteristics of SOTRAS are:

- modular set-up allowing flexible combination of sub-models for water transport, chemical transport, heat transport, geochemical and biochemical reactions etc;
- multi-layer soil column because soils generally show a distinct variation of soil properties with depth and because most pollutants develop a distinct concentration front;
- transient or stationary transport of water, heat and chemicals. Depending on the mobility, stability and application of the chemicals the overall behaviour may be dominated by average or event based soil conditions;
- strict protocols for FORTRAN code layout, data interfaces between modules and input and user procedures; this is necessary to coordinate model application for a variety of problems by a groups of researchers.

Transport programs developed according to the SOTRAS-SiShell standard are primarily meant for the analysis of the behaviour of trace compounds like pesticides (Tiktak *et al.*, 1994b), metals (this report), and volatile organic contaminants (Freijer *et al.*, 1995).

This report describes the general background of transport and reactions of trace metals (chapter 2), the development of the computer program for cadmium (chapter 3), the verification of the speciation and transport submodels using batch and column experiments (chapter 4), a test application for transport and accumulation of cadmium in a forest ecosystem (chapter 5). In chapter 6 some remarks and recommendations are given. A user manual is included in the appendix.

2 BEHAVIOUR AND TRANSPORT OF METALS IN SOILS

The transport and behaviour of heavy metals in soils are extensively described by for example Lindsay (1979), Stumm and Morgan (1981), and Ellis *et al.* (1983). In this chapter a general summary is given. The following metals are potentially considered: copper (Cu), zinc (Zn), cadmium (Cd), mercury (Hg), lead (Pb), chromium (Cr) and nickel (Ni). A model describing the movement of trace metals should describe:

- the distribution of metals over the aqueous and solid phase;
- the transport of metals in the aqueous phase by convection and dispersion;
- the homogenization of soil due to tillage and biological activity;
- uptake and removal of metals by plants and crops.

The importance of homogenization and removal by plants strongly differs between agricultural systems, forests, and low natural vegetations.

Metals can be present in different forms in the solid and aqueous phase of the soil:

- in the matrix of primary minerals, particularly in ferromagnesian minerals and sulfides (eg. Chessworth, 1991);
- in secondary precipitates, eg. carbonates, hydroxides and, in a reduced environment, in sulfides;
- adsorbed to the surface of soil particles, particularly to surface of clay minerals, organic matter and oxides;
- in the soil solution, either as free ions or as complexes with inorganic and organic ligands;
- in exceptional cases, eg. for mercury, metals can occur as gaseous species.

To predict the distribution and concentration of metals in soil, the following processes need to be described:

- speciation, which is the distribution of the dissolved metal over different actual inorganic and organic forms (§2.1);
- adsorption and desorption (§2.2);
- dissolution (weathering) and precipitation (§2.3); and
- transport of metals (§2.4).

2.1 Speciation

Speciation refers to the distribution of a component over all actual forms in the soil solution. Rates of simple speciation reactions are very fast (Stumm and Morgan, 1981), and the establishment of equilibria is therefore assumed to take place instantaneously. For heavy metals the following groups of species are relevant:

- free metals (M^{n+}). All considered trace metals are bivalent,
- inorganic complexes. The most important inorganic ligands are fluoride (F^-), chloride (Cl^-), bromide (Br^-), sulphite (S^{2-}), hydroxyl (OH^-), carbonate (CO_3^{2-}), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and perchlorate (ClO_4^-). The stability of inorganic complexes for metals increases in the following order (Stumm and Morgan, 1981):
  - $F^- > Cl^- > Br^- > S^{2-}$, and
  - $CO_3^{2-} > NO_3^- \,\&\, PO_4^{3-} > SO_4^{2-}$

  The stability for complexes of transition metals and a specific ligand increase from:
  - Cu > Zn, and
  - Cu > Ni

  The stability of hydroxy complexes increases from:
  - Hg > Pb > Cu > Zn > Cd
- organic complexes and chelates. The size, behaviour and stability depends on the molecular weight of the organic ligand. Distinction can be made between simple chelates (1 nm), metal complexes with high molecular weight material like lipids, fulvic acids etc (10 nm) and colloids (>100 nm). For metal complexes with low molecular weight, organic hydroxides, and acids the stability increases from:
  - $OH^- > RO > RCOO$ (where R indicates the hydrocarbon group), and from
  - Hg > Pb > Cd > Zn.

Only dissolved species are mobile and can be transported by dispersion or convection. However, due to speciation the total mobile concentration can be much higher than the free metal concentration. The ratio of total metal over free metal concentrations in fresh water is 2.9 for Cu, 1.05 for Zn, 1.07 for Cd, and 10.5 for Pb (Stumm and Morgan, 1981). Hesterberg *et al.* (1993) inferred ratios of 1 to 10 for Zn and Cd and 1 to 100 for Cu in manure and fertilizer amended agricultural soils. They concluded a predominance of organic, DOC related, complexes. Complexation strongly varied with soil depth and time due to effects of pH. It is often difficult to identify the nature of dissolved organic material in soil solution. Hesterberg *et al.* (1993) defined lumped complexation reactions and constants for natural DOC:

$$M^{m+}_{(aq)} + DOC^{-}_{(aq)} \rightleftharpoons MDOC^{(m-1)}_{(aq)} \tag{1}$$

$$\log K^c = \log \frac{[MDOC^{(m-1)}]}{[M^{m+}]\cdot[DOC^-]} \tag{2}$$

$$\log K^c = n \text{ pH} + b \tag{3}$$

$$\frac{[MDOC^{(m-1)}]}{[M^{m+}]\cdot[DOC^-]} = n \log(OH^-) + 14n + b \tag{4}$$

Hesterberg *et al.* (1993) derived a value of 0.62 for n and 0.30 for b for Zn and 0.26 for Cd. They used fulvic acid as an analogue for DOC.

2.2 Adsorption and desorption

Adsorption and desorption reactions are slower than simple speciation reactions. Chardon (1984) showed for adsorption of Cd that:

- in a peaty soil, at different initial concentrations, the adsorption was completed for 95% within two minutes,
- in experiments with two forest soils the adsorption was completed within 3 to 10 hours of shaking, and
- in experiments with metal additions to two mineral soils, after three hours no decrease of the dissolved concentration toke place, which indicated that sorption was complete.

From this it can be concluded that models assuming equilibrium sorption should not be used to assess variation of dissolved concentrations at higher temporal resolutions than roughly one day.

The binding force for adsorption of metals in general is electrostatic, however structural bidentate binding effects are also relevant. Various types of models have been proposed for adsorption of metals (Felmy *et al.*, 1983; Keizer and Riemsdijk, 1994). Adsorption and desorption mechanisms are described using *constant charge* or *variable charge* models. Variable charge models take into account the interaction between the electrostatic surface charge, the adsorbed species and the soil solution chemistry. Some examples are the Diffuse Double Layer model, the Constant Capacitance model, the Triple Layer model and Basic Stern model. For the application of the variable charge models more specific information is needed on the nature of the adsorbing particle surface, than for the constant charge models. Constant charge models can be more easily fitted to commonly available experimental isotherms or to field observations of adsorbed and aqueous concentrations. In the latter case empirical regressions can be made to relate the adsorption constants to soil properties like pH, organic matter content, CEC and/or ionic strength. For such regressions it is crucial to uniquely define the aqueous and adsorbed concentrations, to avoid confusion between total dissolved metal concentration and free metal concentration, or between total soil concentration, total adsorbed concentration and extractable concentration. Commonly used constant charge models are:

Linear distribution

$$\frac{Q}{c} = K_d \tag{5}$$

where Q (mol kg^{-1}) is the adsorbed metal concentration, c (mol L^{-1}) is the concentration of the metal in the soil solution, and K_d (L kg^{-1}) is the linear distribution coefficient.

Langmuir isotherm

$$Q = \frac{K_L\ Q_{\max}\ c}{1 + K_L\ c} \tag{6}$$

where K_L (L mol^{-1}) is the Langmuir constant, and Q_{max} (mol kg^{-1}) is the maximum adsorbed metal concentration.

Freundlich isotherm

$$Q = K_F\ c^n \tag{7}$$

where K_F (mol^{1-n} kg^{-1} L^n) is the Freundlich adsorption parameter and $1/n$ (-) is the slope of the plot of log(Q) versus log(c). The Freundlich equation is commonly used in models for heavy metal behaviour. In METRAS, an extended Freundlich equation is used (Eqn. (27)).

Ion exchange

$$K_{ex} = \frac{Q_1}{Q_2} \cdot \frac{c_2}{c_1} \tag{8}$$

where K_{ex} is the exchange constant. In principle exchange equations have to be derived for metal ions competing for adsorption sites, and resulting equations have to be solved simultaneously.

2.3 Precipitation and dissolution

Dissolution and precipitation are relatively slow reactions. As a result, natural soil solutions are often strongly under- or supersaturated with respect to theoretically or actually present minerals. The release of trace metals from primary minerals should be regarded as kinetic processes with a constant rate related to the overall dissolution rate of the silicate and the bulk content of heavy metals in the mineral. Precipitation of commonly occurring hydroxides and carbonates is faster but cannot be regarded as equilibrium reactions.

The heavy metals considered in this study can precipitate into or dissolve from oxides, hydroxides, carbonates, and sulfides:

$$\begin{aligned} MO + 2H^+ &\rightleftharpoons M^{2+} + H_2O \\ M(OH)_2 + 2H^+ &\rightleftharpoons M^{2+} + 2H_2O \\ MCO_3 + 2H^+ &\rightleftharpoons M^{2+} + CO_3^{2-} \\ MS &\rightleftharpoons M^{2+} + S^{2-} \end{aligned} \tag{9}$$

The formation and dissolution of these precipitates in general strongly depends on pH and (in the case of sulphite) redox potential. Table 2 summarizes stability constants for the precipitates described in equation (9). Whether these precipitates will actually be formed at a substantial rate is not indicated. If necessary, the originally reported constants for carbonates were recalculated using the carbon dioxide solution equilibrium:

$$CO_{2,g} + H_2O \rightleftharpoons CO_3^{2-} + 2H_2O \qquad \log K = -18.14 \tag{10}$$

The originally reported stability constants are generally written for reduction of SO_4^{2-} and with HS^- as dissolution product instead of S^{2-}. These constants were recalculated using the following two equilibria:

$$HS^- \rightleftharpoons S^{2-} + H^+ \qquad \log K = -12.90 \tag{11}$$

$$SO_4^{2-} + 9H^+ + 8e^- \rightleftharpoons HS^- + 4H_2O \qquad \log K = 33.64 \tag{12}$$

TABLE 2

Logarithms of stability (solubility) constants for common precipitates at 25 °C. The corresponding reactions are described in Eqn. (9).

metal	oxides	hydroxides	carbonates	sulfides
Cd	CdO	β-Cd$(OH)_2$	$CdCO_3$	CdS
	15.14[a] 15.12[d]	13.65[a,c,d] 13.67[d]	-11.99[a] -11.70[c] -13.74[d]	-27.00[c] -28.83[a,b,d]
Cr	CrO_3	$Cr(OH)_2$	$CrCO_3$	CrS
	-3.21[d]	10.82		
Cu	CuO	$Cu(OH)_2$	$CuCO_3$	CuS
	7.66[a] 7.65[c] 7.62[d]	8.68[a] 8.64[b,d]	-9.63[a,b,d]	-36.3[d] -36.1[a,c]
Hg	HgO	$Hg(OH)_2$	Hg_2CO_3	HgS
	2.44-2.48[a] 2.56[c]	2.59[a]	-44.76[a]	β: -72.40[a] α: -71.77[a]
Ni	NiO	$Ni(OH)_2$	$NiCO_3$	
	12.45[d]	10.80[b,d]	-6.84[b,d]	
Pb	PbO	$Pb(OH)_2$	$PbCO_3$	PbS
	12.89[a] 12.98[b,d] 12.91[d] 12.72[a,d]	8.16[a] 8.15[b,d]	-13.50[a] -13.10[c] -13.13[b,d]	-27.51[a,c] -28.03[b,d]
Zn	ZnO	$Zn(OH)_2$	$ZnCO_3$	ZnS
	11.16[a] 11.31[b] 11.14[c]	12.48 (amorphous)[a] 12.19 (α)[a] 12.45 (α)[b] 11.78 (β)[a] 11.75 (β)[b] 11.74 (γ)[a] 11.71 (γ)[b] 11.53 (ε)[a,b]	-10.24[a] -10.26[b] -10.19[c]	-24.70[a] -24.50[a] -21.95[b]

a Keizer and Van Riemsdijk, 1985

b Felmy *et al.*, 1983

c Stumm and Morgan, 1981.

d Appelo and Postma, 1993.

2.4 Transport of metals in soil

Transport of metals in the soil is primarily controlled by convective displacement of soil water. Additionally, diffusion and dispersion processes affect the shape of the infiltrating solute front.

2.4.1 Mass balance

The content of metals in the soil system, c^* (mol m^{-3}) is described as:

$$c^* = \theta c + \rho Q \tag{13}$$

in which c (mol m^{-3}) is the concentration of metals in the liquid phase, θ (m^3 m^{-3}) is volumetric water content, ρ (kg m^{-3}) is dry bulk density of the soil and Q (mol kg^{-1}) is the mass content of metals at the soil solid phase. The mass action equation for sorption is described in more detail in chapter 3.

2.4.2 Vertical transport

The continuity equation for transport of a metal in the soil system reads:

$$\frac{\partial c^*}{\partial t} = -\frac{\partial J_s}{\partial z} + S_s + Dr_s + R_s \tag{14}$$

where c^* (mol m^{-3}) is mass content of a metal in the soil system, J_s (mol m^{-2} d^{-1}) is mass flux of a metal through the soil, S_s (mol m^{-3} d^{-1}) is volumetric uptake rate of a metal, Dr_s (mol m^{-3} d^{-1}) is volumetric net lateral drainage rate of a metal and R_s (mol m^{-3} d^{-1}) is the volumetric rate of non-equilibrium transformation processes in the soil system. Notice that the sink terms S_s, Dr_s and R_s are positive in the case of net flow into the soil column and negative in the case of net flow from the soil column. The mass flux of a metal through the soil is described by:

$$J_s = J_w c - \theta (D_{dis} + D_{dif}) \frac{\partial c}{\partial z} \tag{15}$$

where J_w (m d^{-1}) is the soil water flux and D_{dis} and D_{dif} (m^2 d^{-1}) are the coefficients for dispersion and molecular diffusion. J_w is negative in case of downward transport. D_{dis} is calculated from:

$$D_{dis} = L_{dis} \left| \frac{J_w}{\theta} \right| \tag{16}$$

in which L_{dis} (m) is the dispersion length. Notice that J_w/θ equals the average rate of flow of the pore water, v. D_{dif} is calculated from:

$$D_{dif} = \lambda D_o \tag{17}$$

in which λ (-) is the tortuosity and D_o (m^2 d^{-1}) is the diffusion coefficient in water.

2.4.3 Boundary and initial conditions for the transport model

The user has to specify the initial contents in the soil system, so the initial condition reads:

$$c^*(z,0) = c^*_i(z) \qquad z \leq z_{ref} \tag{18}$$

in which $c^*_i(z)$ (mol m^{-3}) is initial content and z_{ref} is reference height.

The upper boundary condition is a flux boundary condition. The lower boundary condition reads:

$$J_s = \min[(J_w.c),0] \qquad t \geq 0 \qquad z = L \tag{19}$$

Here, L (m) is height at the lower boundary of the system. Equation (19) implies that at the lower boundary only convective flow out of the system is allowed (J_w is negative when waterflow is downward).

2.4.4 Soil water transport

The vertical soil water flux, J_w {eqn. (15)} is calculated with the hydrological model SWIF (Tiktak and Bouten, 1992). A full description of the SOTRAS implementation of this model is found in Tiktak *et al.*, 1994b. METRAS can optionally read long-term average soil water fluxes and soil water contents. In this case, the sink term is calculated for each soil layer as follows:

$$S_i = J_{w,i} - J_{w,i-1} \tag{20}$$

where S (m d^{-1}) is sink term accounting for root water uptake (if $h < 0$) or later drainage (if $h \geq 0$), and i is soil layer index. h (m) refers to soil water pressure head.

3 MODEL DESCRIPTION

3.1 Overview of METRAS

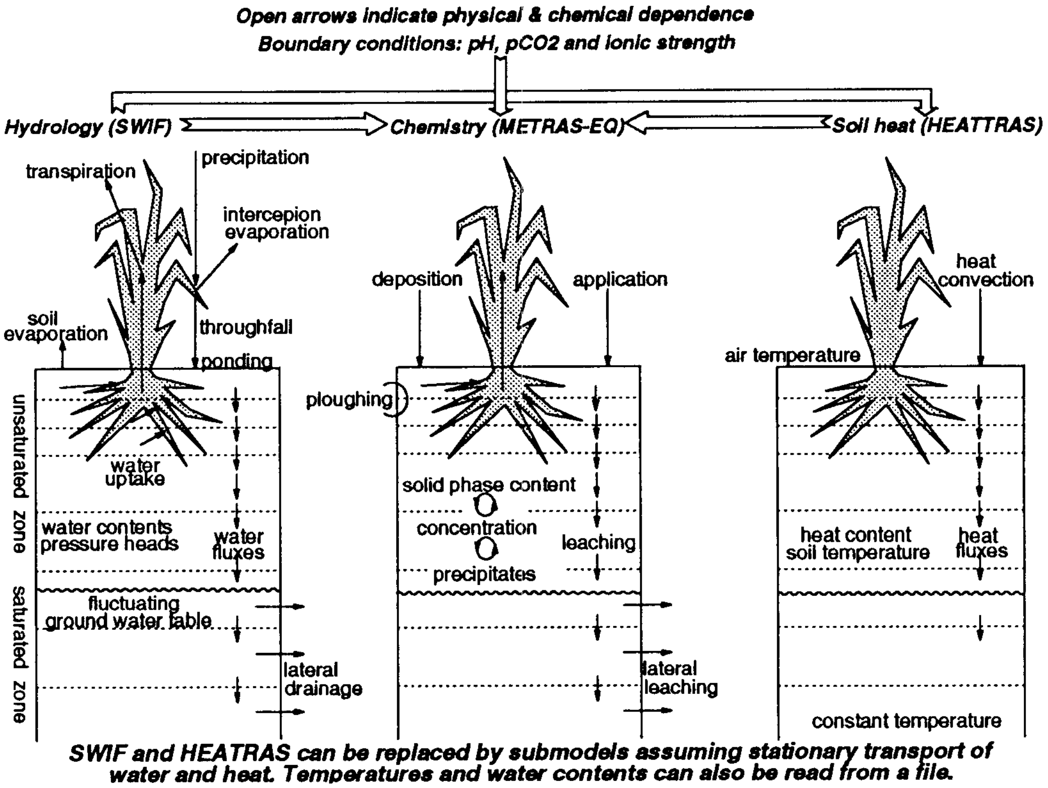
METRAS (METal TRansport ASsessment) is a generic one-dimensional, dynamic, multi-layer model for simulating transport and accumulation of trace metals in the unsaturated soil zone and the uppermost part of the saturated zone. The structure of the METRAS model is similar to that of the PESTRAS model (Tiktak *et al.*, 1994b). The model consists of four major modules: interception and evapotranspiration, soil hydrology, heat transport, and chemical transport and behaviour (Figure 1).

- The daily potential evapotranspiration is calculated from the Makkink equation (Makkink, 1957) and an empirical crop dependent factor. Potential evapotranspiration is divided into the potential evaporation from the soil surface and the potential crop evaporation on the basis of the Leaf Area Index.
- Soil hydrology is simulated by the module SWIF (Tiktak and Bouten, 1992). This module calculates soil water transport according to Darcy's law. The model calculates root water uptake from individual soil layers on the basis of the root length distribution. Root water uptake is reduced by water shortage and anaerobiosis. The model calculates preferential uptake from relatively wet soil layers. Actual evaporation from the soil is calculated by an empirical equation. Lateral drainage is restricted to the saturated soil zone. It is calculated with an empirical function.
- Soil heat transport is simulated by the HEATTRAS module, which is based on the heat exchange algorithm in the ILWAS (Chen *et al.*, 1983) and SOILN-NL (Van Grinsven and Makaske, 1993) models. The module simulates transport of heat by conduction through the solid, liquid and gas phases, and convection by soil water. The upper boundary condition is the daily average air temperature, the lower boundary condition is a constant temperature, which is set equal to the long-term average air temperature. In METRAS this module is used to correct stability constants for temperature.
- Speciation and transport of metals is described in the METRAS-EQ module. The speciation submodel, EQCAD, calculates the daily concentrations and activities of the species. In addition, it calculates the daily mobile concentration of the component, which is the major input for the solute transport module. The transport module takes into account convective and dispersive transport.

The hydrological submodels SWIF and SBOUND, and the soil heat submodel HEATRAS can optionally be replaced by submodels assuming stationary transport of water and heat, respectively. In this case, long-term average fluxes and states for water and heat can be calculated with the stand-alone version of these models.

3.1.1 Flow diagram of the main program

A flow diagram of the main programme of METRAS is presented in Figure 2. The flow diagram reflects the chemical and physical dependencies in the model (see also Figure 1). The transport of metals in the soil depends on soil water fluxes, lateral drainage fluxes and soil water contents. Activity coefficients and stability constants depend on soil temperatures, which are calculated by the soil heat submodel. The transport of heat in the soil is dependent on air temperatures, soil water fluxes and soil water contents. Furthermore, soil water transport depends on infiltration fluxes fluxes and potential evapotranspiration, which are calculated by the interception and evapotranspiration module. Throughfall fluxes and potential evapotranspiration are driven by meteorological variables (precipitation, air temperature and global radiation). pH, ionic strength and partial CO_2 pressure are boundary conditions for the model.



SWIF and HEATRAS can be replaced by submodels assuming stationary transport of water and heat. Temperatures and water contents can also be read from a file.

Figure 1. Overview of the METRAS simulation model.

3.1.2 The metal transport and speciation submodel METRAS-EQ

In the sequel emphasis is placed on the development of the chemistry module for trace metals in general, and for Cd in particular. A major problem with the development of a generic and generally applicable trace metal chemistry module is the potentially large number of chemical reactions in which trace metal may be involved. Accounting for and evaluating these potential reactions is one of the features of general equilibrium models. However, when combining such models with multi-layer transport models, this may lead to overly complex models and excessive run times. Therefore, our point of departure was that, to effectively describe trace metal behaviour in soils, that is for being able to calculate transport and concentrations of major species, only a small number a reaction needs to be considered. The consequence of this system simplification is that solution of the equilibrium problem will become simpler, run times will go down but that the application range of the chemistry model will be restricted. The application purpose was therefore restricted to *non-point sources pollutants*, with relatively low total metal concentrations in the soil and low background electrolyte levels. Examples of such non-point trace metal sources for soil pollution are atmospheric deposition, application of fertilizer, manure and sewage sludge.

3.2 Procedure for development of the speciation submodel

The procedure that was adapted for development of the speciation submodel (EQCAD) was:

1. Use a general equilibrium model to identify the relevant speciation and precipitation reactions for the relevant application range (i.e. non-point source pollutants with low metal and electrolyte concentrations). For this purpose the ECOSAT (Keizer and van Riemsdijk, 1994) and MINEQL+ (Schecher and McAvoy, 1991) models were used.
2. List the relevant mass action and mass balance equations. The general form of the mass action equation is:

   $$K_{i,j} = \prod_{i,j=1}^{n,m} \gamma_{i,j} \, [s_i \, (c_j)]^{a(i,j)} \tag{21}$$

   in which i is species index, j is component index, K is reaction constant, $[s_i]$ is concentration of species i, c_j is component j, γ is activity coefficient of species i, and $a(i,j)$ is stoichiometric coefficient of component j in species i. The general form of the mass balance equation is:

   $$[c_j]_{tot} = \sum_{i=0}^{n} [s_i(c_j)] \tag{22}$$

3. Integrate all equations into one closed form equation. For this purpose the mathematical software package DERIVE was used (Soft Warehouse Inc., 1990).
4. Solve this equation, using the total component concentrations for input, to find the free metal ion concentration. All other species concentrations can next be calculated from the mass action equations.

For deriving the closed form equation only complexation and adsorption reactions were considered, and not precipitation-dissolution reactions. These reactions are only relevant in case the precipitate is actually present as a source for the component, or in case the solution becomes supersaturated with respect to the solid phase. Occurrences of supersaturation or undersaturation are checked after solution of the closed form equation (§3.6). In case the solution is supersaturated, an estimate is made of the amount of the components that can potentially precipitate. Next, the closed form equation is solved with the adjusted estimates of the total component concentrations. This sequential solution of the closed form equation and the solid phase equilibrium is repeated until convergence,

3.3 System description for Cd

The soil chemistry module was first set up for the behaviour of Cd in soils receiving Cd from non-point sources. This particularly applies to forest soils, soils underlying low semi-natural vegetations, and agricultural soils. The following components were considered:

- Cd^{2+}, Cl^-, SO_4^{2-}, OH^- (H^+), CO_3^{2-} and PO_4^{3-};
- adsorption sites for cadmium. The adsorption reaction is described by an adjusted Freundlich isotherm;
- all precipitates involving Cl^-, SO_4^{2-}, OH^-, CO_3^{2-} and PO_4^{3-};
- pH and the partial pressure of CO_2 are constant boundary conditions.

Next the chemical equilibrium model ECOSAT (Keizer and van Riemsdijk, 1994) was applied to this system using the following boundary conditions:

• ionic strength	0.0100 M
• temperature	298.15 °K
• pH range	1.5 - 12
• p_{CO2} range	0.3 - 3 mbar

From this exercise it was concluded that the major species for the previously defined application are Cd^{2+}, $CdCl^+$, $CdSO_4{}^o$, $CdCO_3{}^o$ and adsorbed cadmium. Furthermore precipitation and dissolution of $CdCO_3$ was relevant. Hesterberg *et al.* 1993 clearly showed that also complexation of Cd to Dissolved Organic Carbon is relevant. In this exercise, however, this complexation reaction was not yet considered.

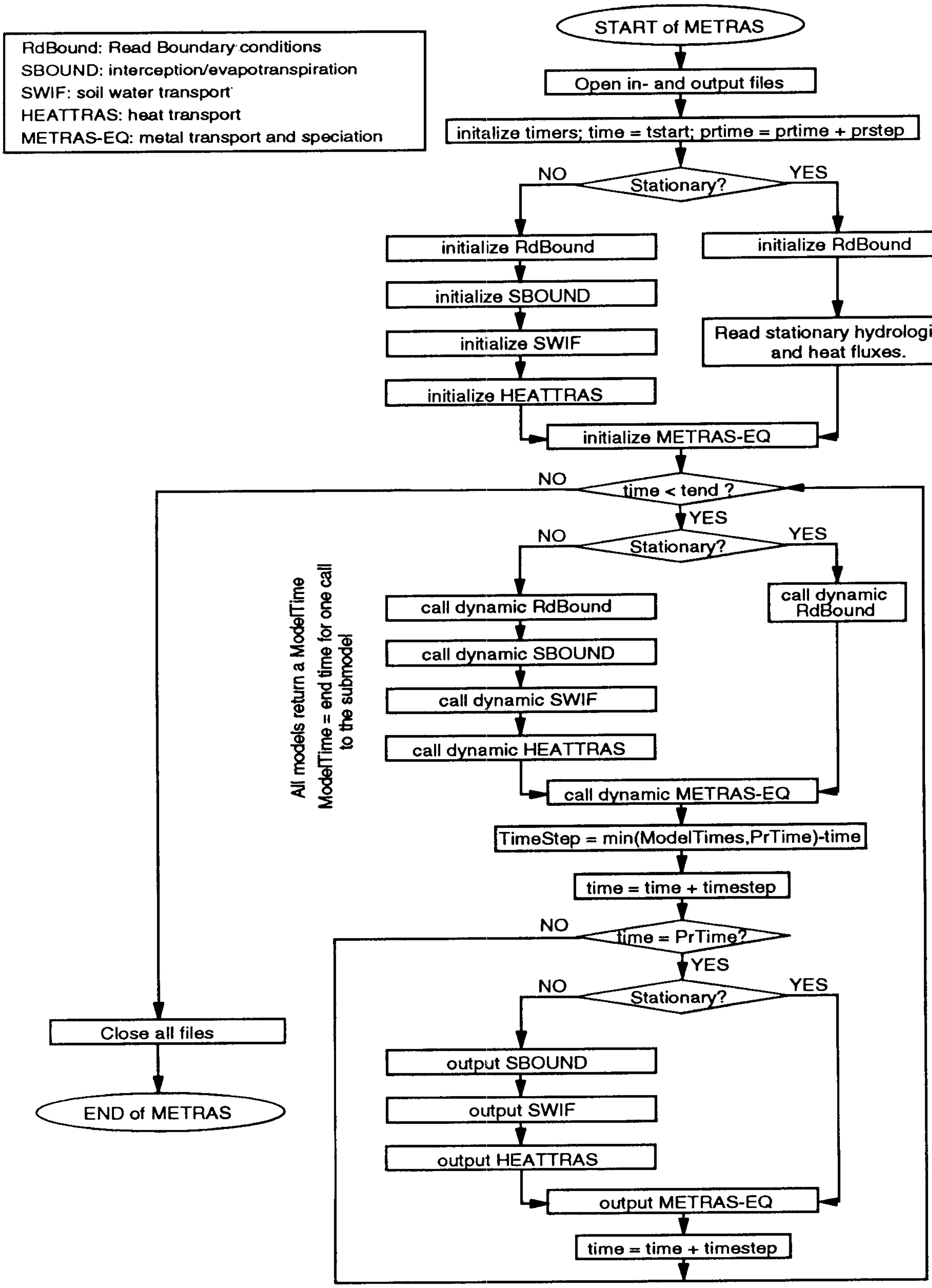


Figure 2 Flow diagram of the main program of METRAS

3.4 Derivation of the speciation submodel for Cd

In the following, sorption sites will be denoted as Q^{2-}, and cadmium adsorbed to the soil will be denoted as QCd. The concentration of species X will be denoted as [X]. The activity of species X will be denoted as (X). Both variables are linked by the activity coefficient f_X:

$$(X) = f_X \cdot [X] \tag{23}$$

Activity coefficients are estimated by the extended Debye-Huckel equation:

$$-\log f_k = \frac{A\, z_k^2 \sqrt{I}}{1 + \mathring{a}_k B\sqrt{I}} \tag{24}$$

where f_k (-) is activity coefficient of ion k, z_k (-) is valence of ion k in solution, I (mol L^{-1}) is ionic strength of the solution, $\mathring{a}$ (Å) is diameter of the ions, and A and B are constants. A and B are proportional to $(\epsilon T)^{-1.5}$ and $(\epsilon T)^{-0.5}$, respectively. Here, ϵ is dielectric constant and T (K) is temperature. At 25 °C A equals 0.51 mol L^{-1}, and B is 0.33 Å $mol^{-0.5}$ $L^{0.5}$. In the actual computer program, constants A and B corrected for temperature are read from a table.

The partial CO_2 pressure (p_{CO2}) and the pH in the soil are boundary conditions of the model. pH and p_{CO2} are linked by the dissolution of CO_2 in water:

$$CO_{2\,gas} + H_2O \rightleftharpoons 2H^+ + CO_3^{2-} \qquad K_{f_{(pCO_2)}} = \frac{(H^+) \cdot (CO_3^{2-})}{p_{CO_2}} \qquad \log K_{f_{(pCO_2)}} = -18.14 \tag{25}$$

In view of the conclusions from §3.3 the following complexation equilibria are considered:

$$\begin{aligned}
&Cd^{2+} + Cl^- \rightleftharpoons CdCl^+ && K_{f(CdCl^+)} = \frac{(CdCl^+)}{(Cd^{2+}) \cdot (Cl^-)} && \log K_{f(CdCl^+)} = 1.98 \\
&Cd^{2+} + SO_4^{2-} \rightleftharpoons CdSO_4 && K_{f(CdSO_4)} = \frac{(CdSO_4)}{(Cd^{2+}) \cdot (SO_4^{2-})} && \log K_{f(CdSO_4)} = 2.45 \\
&Cd^{2+} + CO_3^{2-} \rightleftharpoons CdCO_3 && K_{f(CdCO_3)} = \frac{(CdCO_3)}{(Cd^{2+}) \cdot (CO_3^{2-})} && \log K_{f(CdCO_3)} = 5.40
\end{aligned} \tag{26}$$

Adsorption of cadmium to the soil is described with an extended Freundlich equation (Van der Zee and Van Riemsdijk, 1987):

$$[QCd] = K_{eff}\, (Cd^{2+})^n\, (H^+)^m \tag{27}$$

This mass action equation can be interpreted as a virtual exchange equation:

$$n\,\mathrm{Cd}^{2+} + \mathrm{Q}^{2-} + m\,\mathrm{H}^{+} \rightharpoondown \mathrm{QCd_nH_m^{2-m-2n}} \tag{28}$$

The parameter K_{eff} is a function of the bulk density, the water content, and the organic matter content of the soil. K_{eff} has unusual dimensions. For convenient usage of the model, the constant K^* is introduced. K^* is independent of soil moisture content and bulk density. The following conversion is applied:

$$K_{eff} = K^* \cdot \left(\frac{1}{(10^3 \cdot M_M)}\right)^{1-n} \cdot \frac{{}^{b}\rho_s}{\theta \cdot 10^3} \cdot oc \tag{29}$$

in which K^* ($\mathrm{mg^{1-n}\ L^n\ kg^{-1}}$) is the scaled Freundlich sorption constant, M_x ($\mathrm{g\ mol^{-1}}$) is the molecular weight of metal x, ${}^{b}\rho_s$ ($\mathrm{kg\ m^{-3}}$) is the bulk density of dry soil, θ is volumetric water content ($\mathrm{m^3\ m^{-3}}$), and oc (% by mass) organic carbon content.

For each component a mass balance can be calculated:

$$\begin{aligned}
[\mathrm{Cd}^{2+}]_{tot} &= [\mathrm{Cd}^{2+}] + [\mathrm{CdCl}^-] + [\mathrm{CdSO_4}] + [\mathrm{CdCO_3}] + [\mathrm{QCd}] \\
[\mathrm{Cl}^-]_{tot} &= [\mathrm{Cl}^-] + [\mathrm{CdCl}^+] \\
[\mathrm{SO_4^{2-}}]_{tot} &= [\mathrm{SO_4^{2-}}] + [\mathrm{CdSO_4}]
\end{aligned} \tag{30}$$

Note that the balance for carbon-oxide species is not considered because the system is considered to be open with respect to CO_2.

The equation to be solved to find the $[Cd^{2+}]$ is:

$$[\mathrm{Cd}^{2+}]_{tot} - [\mathrm{Cd}^{2+}] - [\mathrm{CdCl}^-] - [\mathrm{CdSO_4}] - [\mathrm{CdCO_3}] - [\mathrm{QCd}] = 0 \tag{31}$$

By substituting the individual mass action equations into this equation, a function of (Cd^{2+}) follows, which accounts for all relevant reactions, except dissolution and precipitation:

$$\begin{aligned} f\,(\mathrm{Cd}^{2+}) = {} & [\mathrm{Cd}^{2+}]_{\mathrm{tot}} - (\mathrm{Cd}^{2+}) \\ & - K_{eff} \left(f_{\mathrm{Cd}^{2+}}\, (\mathrm{Cd}^{2+}) \right)^{n} \left(f_{\mathrm{H}}\, (\mathrm{H}^{+}) \right)^{m} \\ & - \frac{K_{f\,\mathrm{CdCl}^-}\, f_{\mathrm{Cd}^{2+}}\, f_{\mathrm{Cl}^-}\, (\mathrm{Cd}^{2+})\, [\mathrm{Cl}^-]_{\mathrm{tot}}}{K_{f\,\mathrm{CdCd}^-}\, f_{\mathrm{Cd}^{2+}}\, f_{\mathrm{Cl}^-}\, (\mathrm{Cd}^{2+}) + f_{\mathrm{CdCl}^-}} \\ & - \frac{K_{f\,\mathrm{CdSO}_4}\, f_{\mathrm{Cd}^{2+}}\, f_{\mathrm{SO}_4^{2-}}\, (\mathrm{Cd}^{2+})\, [\mathrm{SO}_4^{\,2-}]_{tot}}{K_{f\,\mathrm{CdSO}_4}\, f_{\mathrm{Cd}^{2+}}\, f_{\mathrm{SO}_4^{2-}}\, (\mathrm{Cd}^{2+}) + f_{\mathrm{CdSO}_4}} \\ & - \frac{K_{f\,\mathrm{CdCO}_3}\, f_{\mathrm{Cd}^{2+}}\, (\mathrm{Cd}^{2+})\, p_{\mathrm{CO}_2}}{K_{f\,p_{\mathrm{CO}_2}}\, f_{\mathrm{CdCO}_3} \left(f_{\mathrm{H}^+}\, (\mathrm{H}^{+}) \right)^{2}} \end{aligned} \qquad (32)$$

After iterative solution of $[\mathrm{Cd}^{2+}]$ from this equation all other species concentrations can be inferred from the individual mass action and mass balance equations.

3.5 Order of computations in submodel METRAS-EQ

Figure 3 shows a flow diagram of the submodel METRAS-EQ. The submodel consists of an interface, an initial section, a dynamic section, and an output section. The initial section is called once from the initial part of the main programme (see §3.1). The dynamic section of the submodel contains a time loop. When entering the submodel, the time is set equal to the global time ('ShellTime', i.e. the time in the main programme), and the end time is set equal to this global time + the time-step in the calling programme ('MetrasTime'). The loop is executed as long as the following expression is true: time < MetrasTime. Notice that the time step in the submodel may be smaller than the time-step in the calling programme. This guarantees flexible coupling of models with different properties. After leaving the loop, time averages for all variables that are in the argument list of METRAS-EQ are calculated. The calculations in the dynamic part are performed in the following order:

- calculation and input of driving variables (e.g. deposition of metals). Note that driving variables that are calculated by other modules within the model (for example soil water contents) are input to the submodel through the argument list.
- calculation of irreversible fluxes (convection/dispersion and lateral drainage fluxes). In METRAS, dispersive and convective fluxes are calculated (see §2.4). Only aqueous species can be transported, viz. Cd^{2+}, CdCl^-, CdSO_4°, CdCO_3°, Cl^- and SO_4^{2-}. The sum of the concentrations for each component, the mobile concentration of each component, is treated as a lumped parameter. These lumped parameters are input to

the transport submodel. Thus, in Eqn. (13)-(19), the following mobile concentrations are considered:

$$\begin{aligned}
[\mathrm{Cd}^{2+}]_{tot} &= [\mathrm{Cd}^{2+}] + [\mathrm{CdCl}^{-}] + [\mathrm{CdSO}_4^{o}] \\
[\mathrm{SO}_4^{2-}]_{tot} &= [\mathrm{SO}_4^{2-}] + [\mathrm{CdSO}_4^{o}] \\
[\mathrm{Cl}^{-}]_{tot} &= [\mathrm{Cl}^{-}] + [\mathrm{CdCl}^{-}]
\end{aligned} \tag{33}$$

The mobile components H^+ and CO_3^{2-} not are explicitly transported. Their concentrations are fixed by the boundary conditions of the model: pH and p_{CO2}.

- integration (calculation of new state variables),
- calculation of speciation of components and precipitation.

This order agrees to the principle of the Continuous Stirred Tank Reactor (CSTR), which is also used in the ILWAS model (Chen *et al.*, 1983).

3.6 Order of computations in the speciation submodel EQCAD

Figure 4 shows a flow diagram of the speciation submodel EQCAD. This chapter briefly discusses some aspects of the computational procedures.

Check whether calculation of speciation is necessary

The submodel EQCAD consumes a major proportion of the total run time of the model (see appendix B). Therefore, before starting a new solution to the speciation problem, the model checks if a new solution is worthwhile in terms of improved accuracy. If the total Cd concentration, $[Cd^{2+}]_{tot}$, is below a user-specified minimum, e.g. the analytical detection limit of cadmium in water, no new iteration is started. In this case all Cd is allocated to QCd, which cannot be transported. If this minimum $[Cd^{2+}]_{tot}$ accuracy parameter is set too low, i.e. in the range of computer precision, incorrect results or even a program crash may follow.

Calculate parameters of the speciation function

The speciation function, Eqn. (32), contains a number of parameters that are time-dependent, in particular soil water content, pH, and soil-temperature. For this reason, the equilibrium constants (including K_{eff}) and the activity coefficients must be recalculated each time-step.

(read further on page 31)

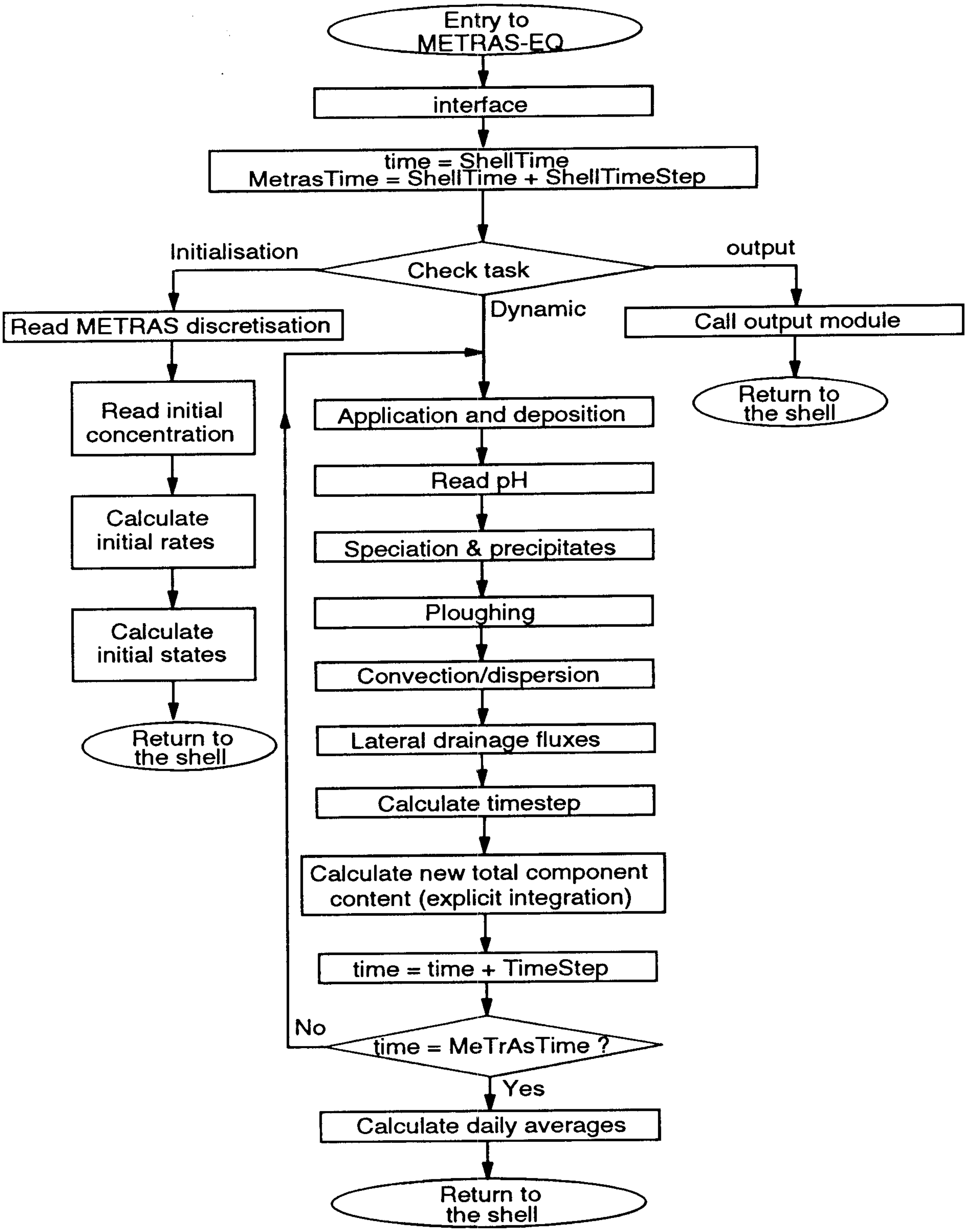


Figure 3 Flow diagram of the submodel METRAS

Solve the speciation function

The root of the Cd speciation function, Eqn. (32), is iteratively determined. Use has been made of an adapted RTSAFE routine of Numerical Recipes (Press *et al.*, 1986). RTSAFE combines the Newton-Raphson and bisection methods. The original RTSAFE routine has been adapted to meet the requirements of METRAS. See appendix B for a full description of the new subroutine.

Calculate concentrations

If the root of the Cd speciation function is found, and $[Cd^{2+}]$ is known, concentrations of all species can be calculated from either the individual mass action equations or component mass balance equations given the total component concentrations.

Precipitation or dissolution

After all species concentrations have been calculated, the model checks for supersaturation or undersaturation with respect to $CdCO_3$. In case the solution is supersaturated, the amount of components forming $CdCO_3$ is estimated. Next the Cd function is solved again with the adjusted estimates of the total component concentrations. This sequential solution of the closed form equation and the solid phase equilibrium is repeated until convergence. When there is solid $CdCO_3$ present, the content of solid $CdCO_3$ is introduced as a new state variable for which a running balance is kept. As precipitation-dissolution reactionns are relatively slow, the reactions will be made rate-limited in a future version of the model. In this case precipitation-dissolution can be treated as a (negative) boundary flux for CO_3^{2-} and Cd^{2+}. As the precipitation rate depends on the degree of supersaturation, this flux must be adjusted each time step.

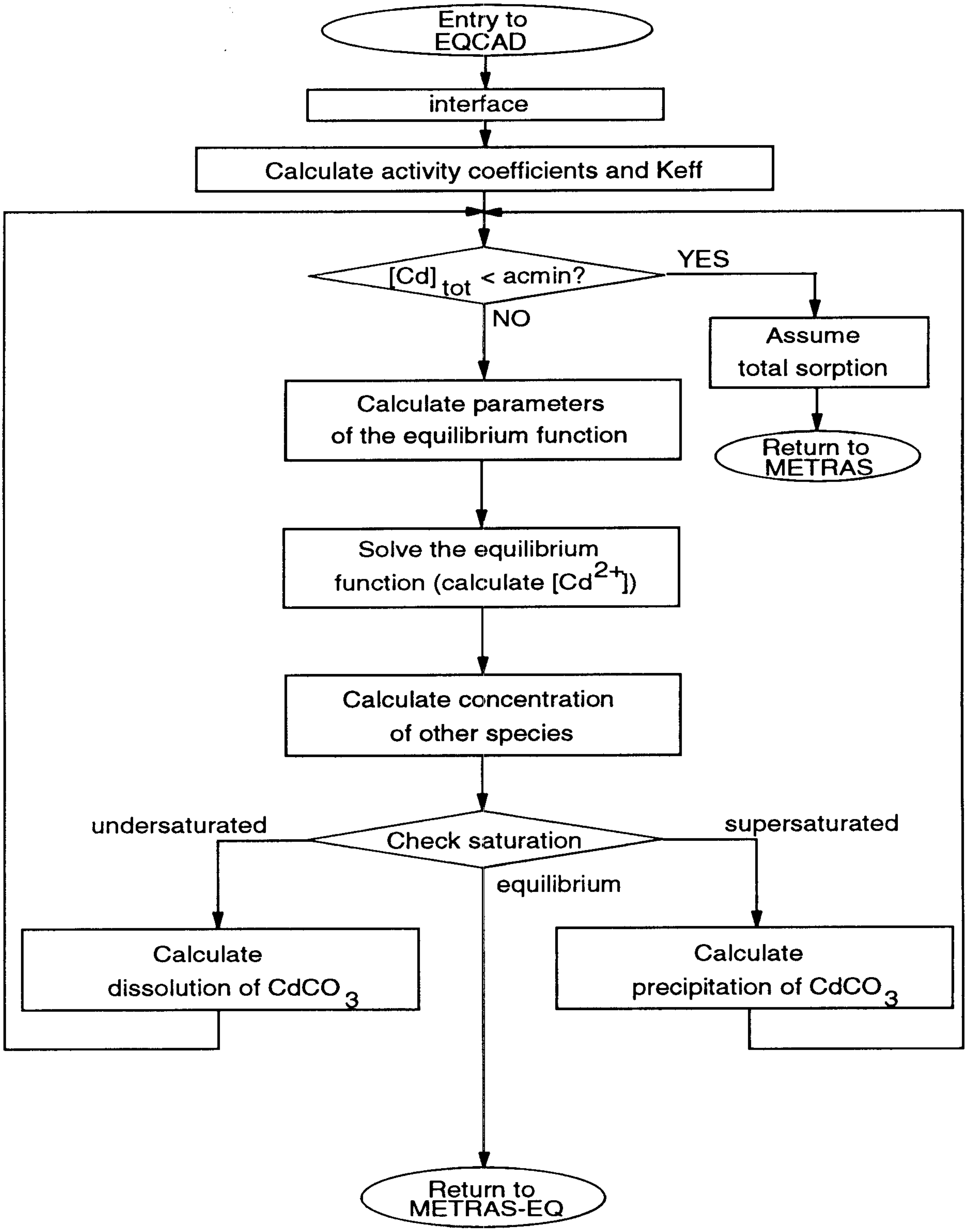


Figure 4 Flow diagram of the speciation submodel of METRAS, EQCAD.

4 APPLICATION OF METRAS TO LABORATORY EXPERIMENTS

METRAS was applied to a well described batch and column experiment for Cd (Boekhold and Van der Zee, 1992). The aim of this application was to verify the correct combination of the general transport submodel, and the speciation submodel.

Boekhold and Van der Zee used soil material from an arable field in the 'Kempen' region in the Southern part of the Netherlands. The soil was a sandy soil with a humic upper layer of 0.25 to 0.30 m, which was classified as a Typic Haplaquod (Soil Taxonomy). Natural cadmium contents in the parent material are negligible. At 1 m intervals two hundred 0-20 cm soil samples were taken with an auger along a transect in the field. The soil samples were air dried and sieved to remove particles larger than 2 mm. The organic matter content was determined by a $K_2Cr_2O_7$ oxidation. Total Cd contents (0.43 M HNO_3 extraction) ranged from 2 to 6 mg kg^{-1}, while bioavailable Cd contents (0.01 M $CaCl_2$ extraction) ranged from 0.2 to 0.8 mg kg^{-1}.

Freundlich adsorption isotherms were determined using batch experiments with 0.005 M and 0.01 M $CaCl_2$ solutions, respectively. Soil was shaken head over end for 20 hours, and the pH was measured in the suspension. The Freundlich isotherm, eqn. (7), was fitted to the sorption data by nonlinear regression (Figure 5; lines 'fitted by Boekhold'). The obtained parameters, K_F and n are different for both cases (0.005 M $CaCl_2$ and 0.01 M $CaCl_2$; see also §4.2).

Breakthrough curves were determined by percolating soil columns of 0.11 m length and 0.016 m diameter with a 0.005 M $CaCl_2$ solution at a flow rate of approximately 1 m d^{-1}. Cd concentrations were 2 or 20 mg L^{-1}, whereby a total number of 160 or 100 pore volumes were displaced.

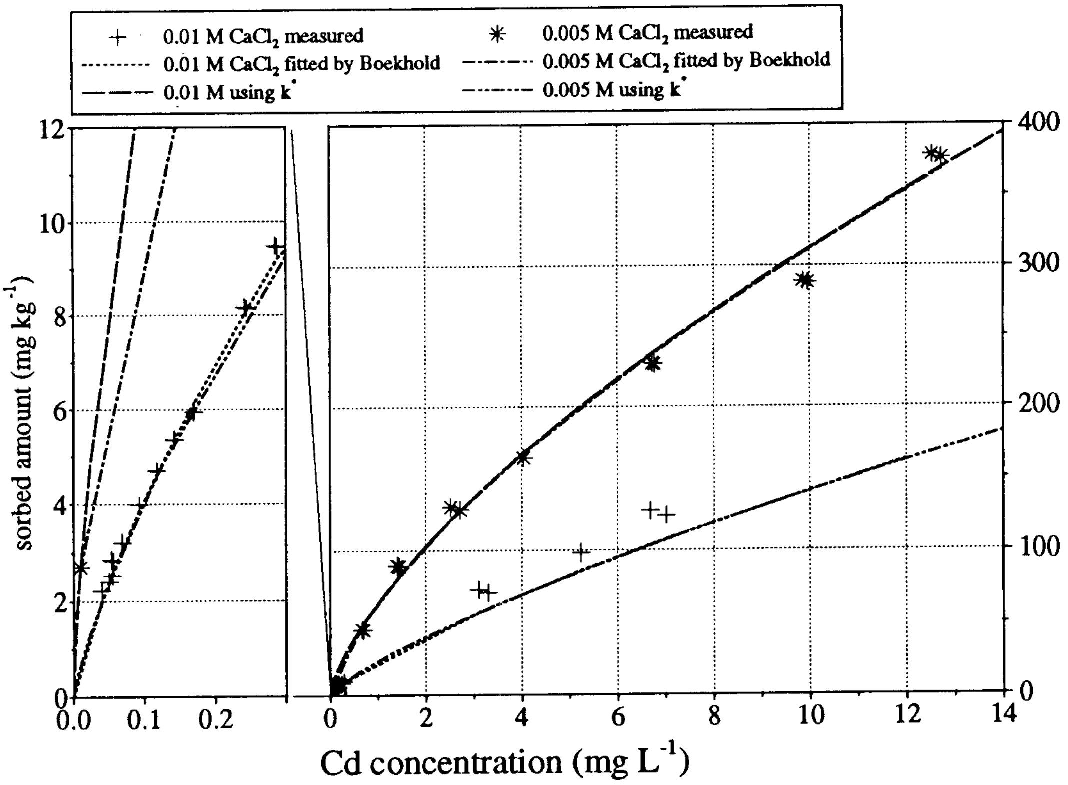


Figure 5 Measured and fitted adsorption isotherms for the low (left) and high concentration ranges (right). For differences between the fittings: see text in §4.2.

4.1 Simulation of breakthrough experiments

The above described column experiments were simulated with METRAS. By doing so, the combination of the equilibrium submodel for Cd, and the general transport submodel was verified. The transport submodel alone has already been verified with an analytical solution by Tiktak *et al.*, 1994. The following parameters were input to the model:

- Water flow was assumed stationary, with a soil water flux of 1 m d^{-1}, and a volumetric soil water content, θ, of 0.41 m^3 m^{-3}. The latter was obtained from measurements on a total number of four soil columns.
- pH was 5.4, and the temperature was 18 °C.
- The dispersion length, θ, was set equal to 0.002 m. The dispersion length was obtained using data of a breakthrough experiment with a conservative tracer (chloride). The derivation of the dispersion length is described in appendix C.
- The diffusion coefficient of all components in water, D_0, was set to 0.4 10^{-4} m^2 d^{-1}, whereas the tortuosity factor, λ, was set equal to 0.363.

Boekhold and Van der Zee fitted a Freundlich equation (Eqn. (7)) to the measured sorption data. With a 0.005 M CaCl$_2$ solution, they obtained a value of 63.7 mg^{1-n} kg^{-1} L^n for K_F, and 0.69 for n. Using these parameters they simulated the breakthrough experiments, and found that both the time of 50% breakthrough, and the time of first breakthrough came too early. For this reason, they replaced the equilibrium sorption model with a kinetic sorption model:

$$\frac{\delta Q}{\delta t} = k_r \left(K_F c^n - Q\right) \tag{34}$$

Here, Q (mg kg^{-1}) is sorbed amount, c (mg L^{-1}) is concentration in the soil solution, K_F (mg^{1-n} kg^{-1} L^n) and n (-) are Freundlich sorption parameters, t (d) is time, and k_r (d^{-1}) is first order rate parameter, which defines to what degree local equilibrium between solution concentration and adsorbed concentration is reached. This kinetic Freundlich sorption model gave a better description of Cd breakthrough.

In METRAS, an equilibrium sorption model is included. The major reason for not including kinetics in the sorption model is that METRAS was designed for field situations, where flow rates are much smaller, and processes are closer to equilibrium than in laboratory experiments with high flow rates. To simulate the above described breakthrough experiments, other Freundlich sorption parameters must be used. These parameters can be directly derived from the two breakthrough experiments described above by assuming stationary flow. First, the retardation factor, R, at the time of 50% breakthrough was read from the measured breakthrough curves (Figure 6), and was 85 for the low (2 mg L^{-1}), and 35 for the high (20 mg L^{-1}) concentration case. The retardation factor, R (-), is defined as:

$$R = 1 + \frac{{}^b\rho_s}{\theta}\frac{\mathrm{d}Q}{\mathrm{d}c} \tag{35}$$

By substituting the first derivative of the Freundlich equation (Eqn. (7)) with respect to c:

$$\frac{\mathrm{d}Q}{\mathrm{d}c} = n\, K_F\, c^{(n-1)} \tag{36}$$

into eqn. (35), the following equation is obtained:

$$R = 1 + \frac{{}^b\rho_s}{\theta}\, n\, K_F\, c^{(n-1)} \tag{37}$$

By substituting ${}^b\rho_s$, θ, and R at c=0.5c_0 for both the low, and the high concentration cases, two equations with K_F and n as unknown variables can be derived. It follows that K_F is 33.72 mg^{1-n} kg^{-1} L^n, and n is 0.61. METRAS uses a scaled Freundlich sorption parameter, K^* (eqn. (29)). By substituting K_F into eqn. (29), K^* can be calculated. With an organic matter content of 2.5%, and a pH of 5.4, K^* is 0.0269 mg^{1-n} kg^{-1} L^n.

Figure 6 shows the measured and simulated breakthrough curves. The dispersion length was obtained from the breakthrough curve of a conservative tracer (chloride). See appendix C for a detailed discussion on this subject. The kinetic sorption model by

Boekhold and Van der Zee (1992) describes both the time of first breakthrough, and the time of 50% breakthrough reasonably well. The time of 50% breakthrough is also simulated reasonably well by METRAS, but the spread of the measured breakthrough curve is higher. Both the asymmetric shape, and the higher spread of the measured breakthrough curves indicate that non-equilibrium conditions prevailed (Boekhold and Van der Zee, 1992). For this particular application, the lack of a kinetic sorption model in METRAS is a serious problem. However, it has never been our intention to apply the model to situations with very high water fluxes (1 m d^{-1}). METRAS was designed for field situations, where flow rates are much smaller, and processes are closer to equilibrium. Unfortunately, on the basis of this experiment, the model can neither be falsified or verified for field conditions.

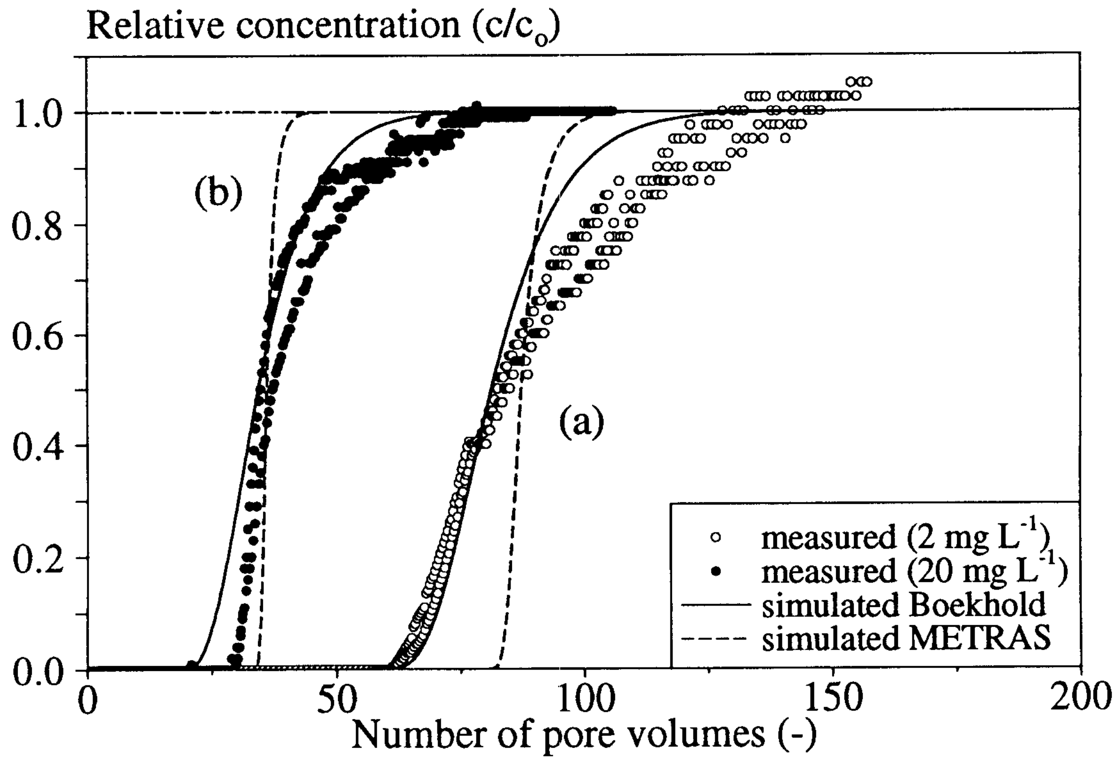


Figure 6 Breakthrough curves of cadmium, measured in duplicate and simulated with a kinetic sorption model (Boekhold and Van der Zee, 1992) and with METRAS, for c = 2 mg L^{-1} (a) and for c = 20 mg L^{-1}.

4.2 Derivation of uniform sorption parameters

The sorption of Cd onto the soil solid phase is affected by pH (García-Miragaya and Page, 1978; Boekhold and Van der Zee, 1992), organic matter content (Adriano, 1986; Boekhold and Van der Zee, 1992), contents of other metals competing for sorption sites (Chardon, 1984), and the ionic strength of the soil solution. Sorption experiments are often conducted under different experimental conditions. Therefore, the obtained sorption parameters have a limited applicability, and must be used carefully.

The effect of pH and organic matter content on sorption of Cd is described in Eqn. (27)-(29). Boekhold and Van der Zee (1992) fitted equation Eqn. (7) to the sorption data (Figure 5; lines 'fitted by Boekhold'), and substituted the obtained parameters into Eqn. (27)-(29). They found that the scaled sorption parameter, K^*, is indeed almost independent of pH and organic matter content. We verified whether Eqn. (27)-(29) could also describe the experimental sorption data directly. Figure 5 shows that this is indeed the case (lines 'using K^*').

Boekhold and Van der Zee (1992) observed differences in K^* when another electrolyte concentration was used (K^* was 0.051 $mg^{1-n}\ L^n\ kg^{-1}$ for the 0.005 M $CaCl_2$ sorption experiment, K^* was 0.024 $mg^{1-n}\ L^n\ kg^{-1}$ for the 0.01 M $CaCl_2$ experiment). This is partly attributed to differences in the activity of free cadmium in the soil solution. To account for this effect, in METRAS the activity coefficient is explicitly taken into account into the extended Freundlich equation:

$$Q = K^{*\prime}\ oc\ (\mathrm{H}^+)^{-0.5} (f_{K,Cd}[\mathrm{Cd}^{2+}])^n \tag{38}$$

where $f_{K,Cd}$ (-) is activity coefficient for Cd, and $k^{*\prime}$ is activity based scaled Freundlich parameter. The other parameters are described in §3.4. The activity based $k^{*\prime}$ is related to the concentration based k^* as follows:

$$K^{*\prime} = \frac{K^*}{(f_{K,Cd})^n} \tag{39}$$

Figure 7 shows fitted adsorption isotherms at the two considered electrolyte levels (0.005 M $CaCl_2$ and 0.01 M $CaCl_2$):

- Using the Freundlich equation as described by Boekhold and Van der Zee (1992). They fitted the Freundlich isotherm at both electrolyte levels independently to obtain two different values for K^*.
- Using the activity based Freundlich adsorption isotherm. One set of parameter values was obtained for both electrolyte levels.

The figure shows that the fit by Boekhold and Van der Zee (1992) gives a better description than the fit based on one parameter set. Apparently, the effect of ionic strength *alone* cannot explain the differences between the sorption experiments.

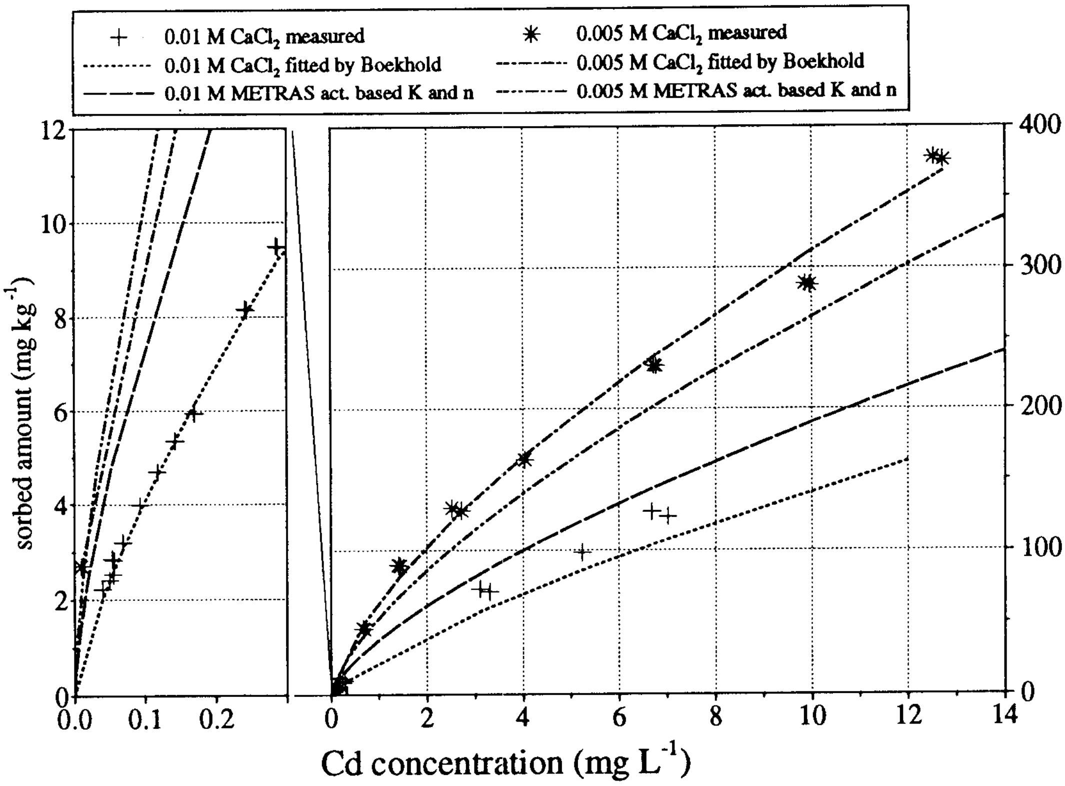


Figure 7 Measured and fitted adsorption isotherms at different electrolyte levels. The sorption parameters were corrected for the influence of ionic strength. See further text.

The concentration of Ca^{2+} in the soil solution is another important factor for sorption of Cd. Bril (personal communication, 1994) corrected the effective sorption parameter for the effect of Ca^{2+}:

$$k^{*''} = k^{*'} (f_{K,\mathrm{Ca}} [\mathrm{Ca}^{2+}])^{(-0.5n)}$$
$$k^{*''} = \frac{k^*}{(f_{K,\mathrm{Cd}})^n} (f_{K,\mathrm{Ca}} [\mathrm{Ca}^{2+}])^{(-0.5n)} \tag{40}$$

where $k^{*''}$ is the corrected k^*. Using this corrected adsorption parameter, the sorption isotherm now shows a rather good fit to the experimental data (Figure 8), and both sorption experiments can now be described using one uniform set of sorption parameters.

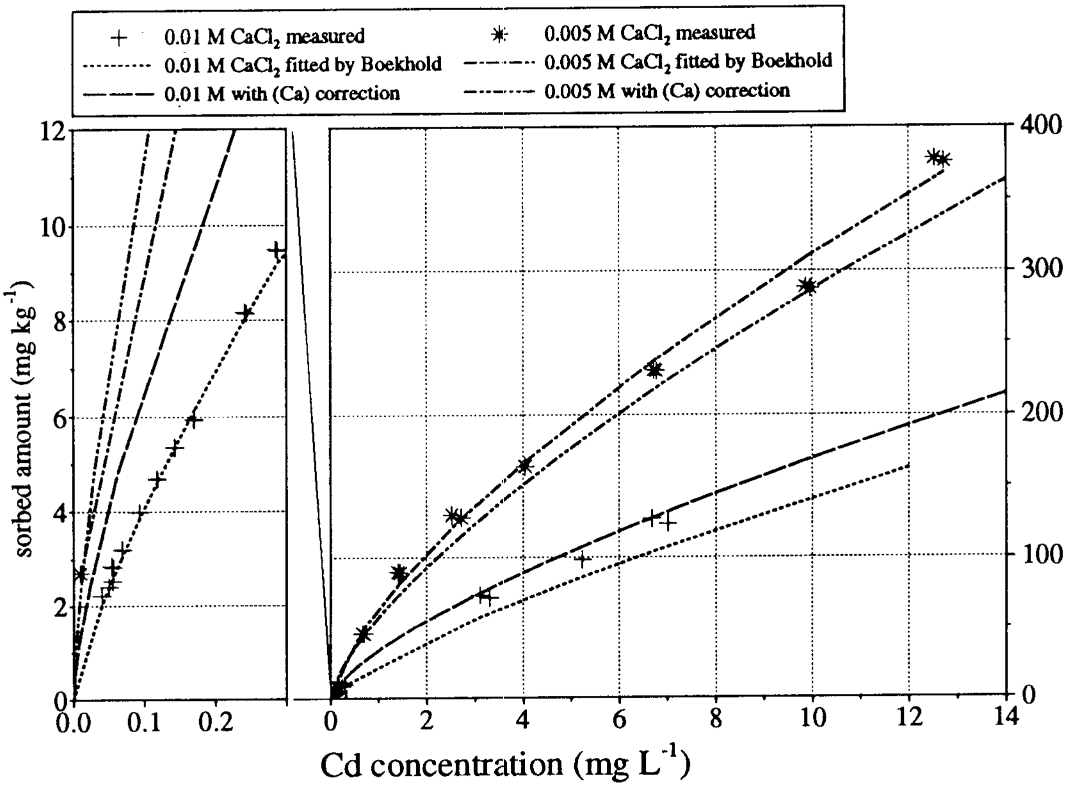


Figure 8 Measured and fitted adsorption isotherms at different electrolyte levels. The sorption parameters were corrected for the effect of $[Ca^{2+}]$. See further text.

4.3 Simulation of titration experiments

A number of hypothetical titration experiments were carried out, to verify the correctness of the speciation submodel in a wider range of pH and total Cd concentration than could be verified from actual batch and column experiments. In these calculations transport was not considered. In a first titration experiment, the pH was adjusted stepwise. The characteristics of the simulated system were:

- total cadmium concentration was 1 mmol L^{-1},
- total chloride concentration was 1.13 mmol L^{-1},
- total sulphate concentration was 0.781 mmol L^{-1},
- temperature was 15° Celsius,
- ionic strength was 0.005 mol L^{-1},
- partial carbon dioxide gas pressure was 3.0 mbar,
- k^{*}'' was 0.597, and n was 0.7.

In a second simulation, the concentration of cadmium was changed stepwise, while the pH was kept constant at 8.5.

Results of both simulations are presented in Figure 9. The first simulation shows that at pH 10.5 $CdCO_3$ starts precipitating and quickly becomes the dominant Cd form. For pH below 10.5, adsorbed Cd was the dominant form. The second titration experiment shows a gradual increase of the amount of sorped cadmium. Results of both simulations compare well with simulations with the chemical equilibrium submodel ECOSAT.

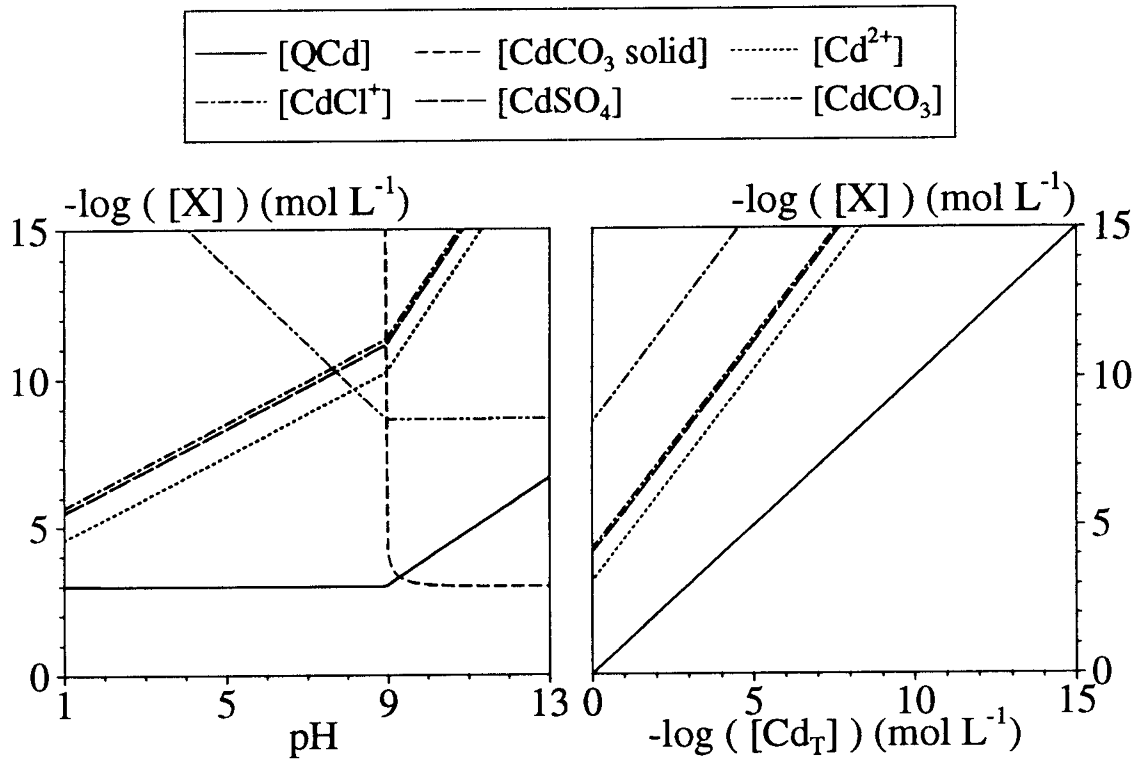


Figure 9 Titration experiments simulated with METRAS, showing the effect on speciation of stepwise increment of pH (left), and $[Cd_T]$ (right).

5 APPLICATION OF METRAS TO A FIELD SITUATION

5.1 Introduction

The application of METRAS to simulate transport and accumulation of Cd for 'De Kempen' region was meant to be an applicability test and a first step towards validation of the model. The point of departure was that METRAS has been developed for analysing problems related to non-point source pollution of soil and groundwater by heavy metals. A further assumption was that the Cd pollution problem in 'De Kempen' region is a representative example of non-point source pollution by heavy metals and that the availability of data is not abnormal. In this perspective the application had several aims:

- qualitatively verify the correctness of the model equations and those model parameters which are independent of the site application.
- investigate if METRAS is applicable to calculate accumulation and leaching of Cd in soils due to long-term atmospheric deposition. Applicable means:
    - can the necessary, case dependent, input parameters (deposition fluxes, adsorption isotherms etc.) be derived.
    - can the present levels of Cd accumulation and leaching be reconstructed on the basis of estimated historic deposition data and soil parameters. Before start of the application it was known that available observations of Cd concentrations in soil and groundwater, estimated deposition fluxes, soil physical data and adsorption isotherms did apply to different sites. This implied that the reconstruction could only be approximate.
- indicate which METRAS parameters were most uncertain and most sensitive for a typical application like the one for 'De Kempen'.
- judge if the application of METRAS to a typical case like 'De Kempen' is reliable enough to allow prediction of future accumulation and leaching of Cd.

5.2 Site description and scenarios

5.2.1 Strijper Aa site

The Strijper Aa area is a coversand area in 'De Kempen', which is situated in the southern part of the Netherlands. This area has received substantial atmospheric loads of Zn and Cd since nearly a century originating from nearby zinc smelters. From various publications (Pedroli, 1988; Maasdam, 1990; Pedroli, 1990) a fairly complete set of soil physical and soil chemical characteristics could be derived for a forest site in Strijper Aa (TABLE 3), including the cadmium concentration of the litter and the soil. The cadmium concentrations in groundwater were taken from a separate study by Boumans and Fraters (1993). The groundwater concentration at the Strijper Aa site was 0.16 μmol L^{-1}, which is the arithmetic mean of five observations in the Strijper Aa study area, with concentrations ranging from 0.08 to 0.28 μmol L^{-1}, and groundwater depths ranging from 1.1 to 4.0 m.

TABLE 3
Soil profile description

Horizon	Depth	Texture[a]	Org. matter	CEC	pH			Cd-extr.[b]	Cd-tot.[c]
	(cm)		(%)	(meq/100g)	(KCl)	(H_2O)	($CaCl_2$)	(mg/kg)	(mg/kg)
L + F1	+9.5 – +6.0	NA	99	17	3.45	4.07	3.62	1.2	1.7
F2 + F3	+6.0 – 0.0	NA	93	23	2.79	3.78	3.06	1.8	5.1
Ah/E	+0.0 – -2.5	VFS	6.1	4.2	2.84	3.63	2.89	0.1	0.3
B/C[d]	-2.5 – -58	VFS	2.9	2.7	4.09	4.26	3.91	< 0.1	< 0.1
BC	-58 – -118	VFS	0.7	0.6	4.49	4.62	4.35	< 0.1	< 0.1
C1	-118 – -168	VFS	< 0.1	1.7	4.27	4.44	4.15	< 0.1	< 0.1
C2	-168 – -186	LVFS	< 0.1	2.3	4.08	4.17	3.90	< 0.1	< 0.1
C3	-186 – -210	VFS	< 0.1	1.0	4.27	4.34	4.06	< 0.1	< 0.1
C4	-210 – -217	LVFS	< 0.1	1.9	4.12	4.26	3.97	< 0.1	< 0.1
C5	-217 – -222	LVFS	< 0.1	2.4	4.01	4.16	3.88	< 0.1	< 0.1
C6	-222 – -270	LVFS	< 0.1	1.3	4.25	4.26	4.00	< 0.1	< 0.1
C7	-270 – -300	LMFS	< 0.1	1.6	4.15	4.24	3.93	< 0.1	< 0.1
C8	-300 – -360	MFS	< 0.1	1.4	3.92	4.22	3.92	< 0.1	< 0.1
C9	-360 – -390	MFS	< 0.1	2.0	3.97	4.17	3.86	< 0.1	< 0.1

[a] NA = not applicable, LVFS – loamy very fine sand, MFS = medium fine sand.
[b] Cd-extr. extraction of the soil with 0.001 $mol.l^{-1}$ Na_2H_2-EDTA (pH 3.46).
[c] Cd-tot. destruction with HNO_3-H_2O_2.
[d] Mixture of broken up podzol horizons.

Historic cadmium deposition and sulphate deposition, as well as the historic development of soil pH are highly uncertain. Also the Cd-adsorption isotherms for the litter layer and deeper mineral soil layers were not available. For these reasons the assessment of Cd accumulation with METRAS was tackled by simulating a range of scenarios, in which these uncertainties were incorporated.

5.2.2 Atmospheric deposition of cadmium

De Kempen area has received Cd deposition originating from smelters in Budel in the Netherlands and from smelters in Belgium. Emissions from the Belgian smelters were not considered, but were probably smaller as Zn production in these smelters was lower and the distance to Strijper Aa is larger. Between 1893 and 1974 the smelter at Budel used a thermal production to extract Zn from the ores, which led to relatively high emissions of zinc and cadmium. In 1974 the factory switched to an electrolytic process which compared to the thermic process had almost negligible cadmium emissions. The estimated total cadmium emission in air, based on the total Cd budget for the factory, was 60-180 tons (Haskoning, 1985). The total Cd deposition was estimated at 50 tons from a survey of Cd contents in the soil in the polluted area (165 km^2) surrounding the smelter (Haskoning, 1985).

The total deposition between 1893 and 1974 at the forest site in the Strijper Aa study area can be estimated in various ways:

- it can be estimated from the observed total soil contents in 1988 (TABLE 3) under the implicit assumption that leaching from the litter layer and the Ah horizon is negligible. This assumption was considered justifiable as the total Cd contents below 2.5 cm depth are below the detection limit. Using this method, the total Cd deposition was estimated at *0.5 kg ha^{-1}*.
- it can be estimated from regional surveys of Cd contents in the soil surrounding the smelter. Using this method, the total Cd deposition amounts to *4.5-7.9 kg ha^{-1}* (Haskoning, 1985; Budelco, 1990; Denneman *et al.*, 1987).

These data show that the historic deposition of Cd onto the Strijper Aa forest area is highly uncertain. In a first step, the lower estimates of deposition (0.5 kg ha^{-1} or 0.448 mmol m^{-2}) were taken for constructing Cd deposition scenarios for the following to two reasons:

- the site appears to be rather unpolluted as shown by total soil contents (TABLE 3).
- the site is situated at the boundary of the polluted area as shown by iso-lines of Cd contents in the soil (Budelco, 1990). Nevertheless, the uncertainty in Cd deposition should be considered.

Based on the lower estimates of deposition, the following two Cd deposition scenarios were developed:

1 A constant annual deposition of 6 µmol m^{-2} a^{-1}.
2 A variable annual cadmium deposition proportional to the zinc production of the factory (Haskoning, 1985; Ros *et al.*, 1987; Meijer *et al.*, 1990; Aben *et al.*, 1991; Aben *et al.*, 1994).

In the second case, the cadmium emission and deposition after 1974 is assumed negligible (Figure 10).

5.2.3 Atmospheric deposition of sulphate

Sulphate is the most important inorganic complexing anion. This complexation reaction may be relevant for Cd mobility. In view of the uncertainty of the historic sulphate deposition, two scenarios were considered:

1 A scenario assuming a constant deposition of 0.148 mol m^{-2} a^{-1} for the entire period.

2 A deposition scenario 'European Renaissance', which has also been input to the model ReSAM (Figure 11) for the period 1950-2010. The deposition between 1893 and 1950 was assumed to be constant, and was set equal to the value for 1950.

5.2.4 Soil pH

The atmospheric deposition of sulphur and nitrogen compounds has led to a decrease of soil pH during the last century. As the adsorption, speciation and precipitation of Cd is strongly pH dependent, METRAS was applied to the Strijper Aa site using two different scenarios for soil-pH development:

1 The pH-$CaCl_2$ observed in 1988 (TABLE 3) was assumed to be valid for the entire simulation period (i.e. 1893-2010).

2 A scenario based on simulations with the general soil acidification model ReSAM (De Vries *et al.*, 1991), and estimates for the initial pH in 1893 (Figure 11). The initial pH was set to 5 for the mineral layers and 3.5 for the litter and the uppermost mineral soil layer. The pH between 1950 and 2010 were based on ReSAM simulations for a neighbouring Scots pine stand on a Gleyic Podzol. pH between 1893 and 1950 was obtained by linear interpolation.

5.2.5 Cadmium adsorption isotherms

The cadmium adsorption isotherms were obtained from Boekhold (1992), who fitted the isotherms with a Freundlich model (Eqn. (27)). The soil material used by Boekhold was taken from an arable field 3 km North-West of a zinc smelter in Neerpelt (Belgium). The plot at Strijper Aa is a forested plot with an almost similar geological background. However, the different land-use history may have consequences for the sorption behaviour of the organic matter and the validity of the adsorption isotherm. Nonetheless, for application of METRAS, this adsorption isotherm was used and applied to the litter layer (organic matter content of about 95%), the upper mineral soil (organic matter content of about 4.5%), and the mineral subsoil (organic matter content <0.1 - 0.7%). To verify the applicability of Boekhold's adsorption isotherms, these isotherms were compared to isotherms obtained by Van der Meijden (1987), Sânchez-Martín and Sânchez-Camazano (1993), Schulte and Beese (1994), and Reinds *et al.* (1994). These isotherms cover different soils with a wide range of organic matter content, clay content and pH. In general, these adsorption isotherms show large differences (Figure 12), introducing a great deal of uncertainty. Therefore, the following runs were performed:

1 A run using the Freundlich adsorption isotherm obtained by Boekhold (1992),

2 A run with a Freundlich coefficient that was divided by three, and

3 A run with a Freundlich coefficient that was multiplied by three.

This range of uncertainty is in accordance with findings of Van der Meyden (1987).

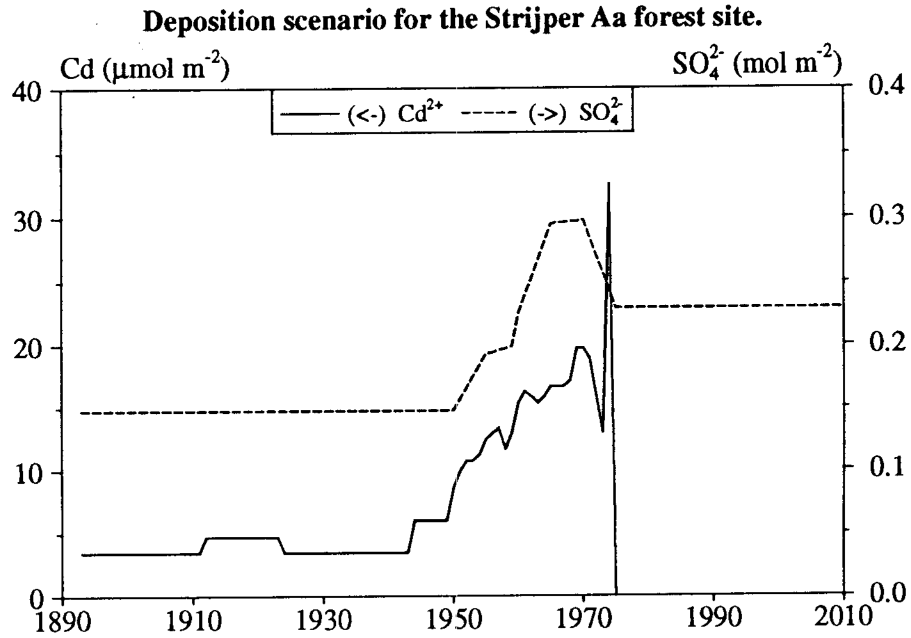


Figure 10 Atmospheric deposition of total Cd (scenario 2) and sulphate (scenario 2) at the Strijper Aa site. See further text.

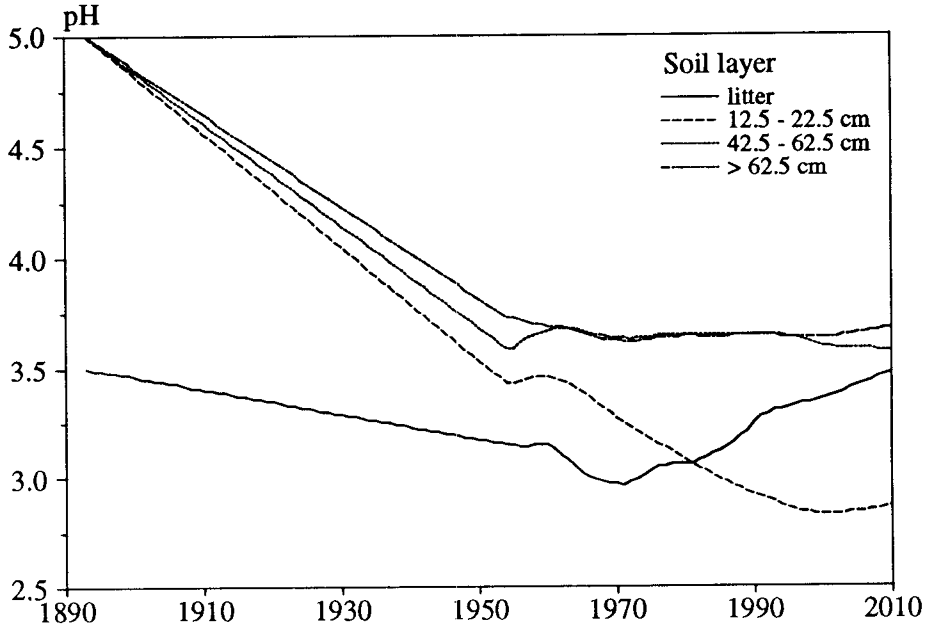


Figure 11 Trends of soil solution pH based on calculations with the model ReSAM for the period 1950-2010, and on linear interpolation for the period before 2010 (scenario 2). See further text.

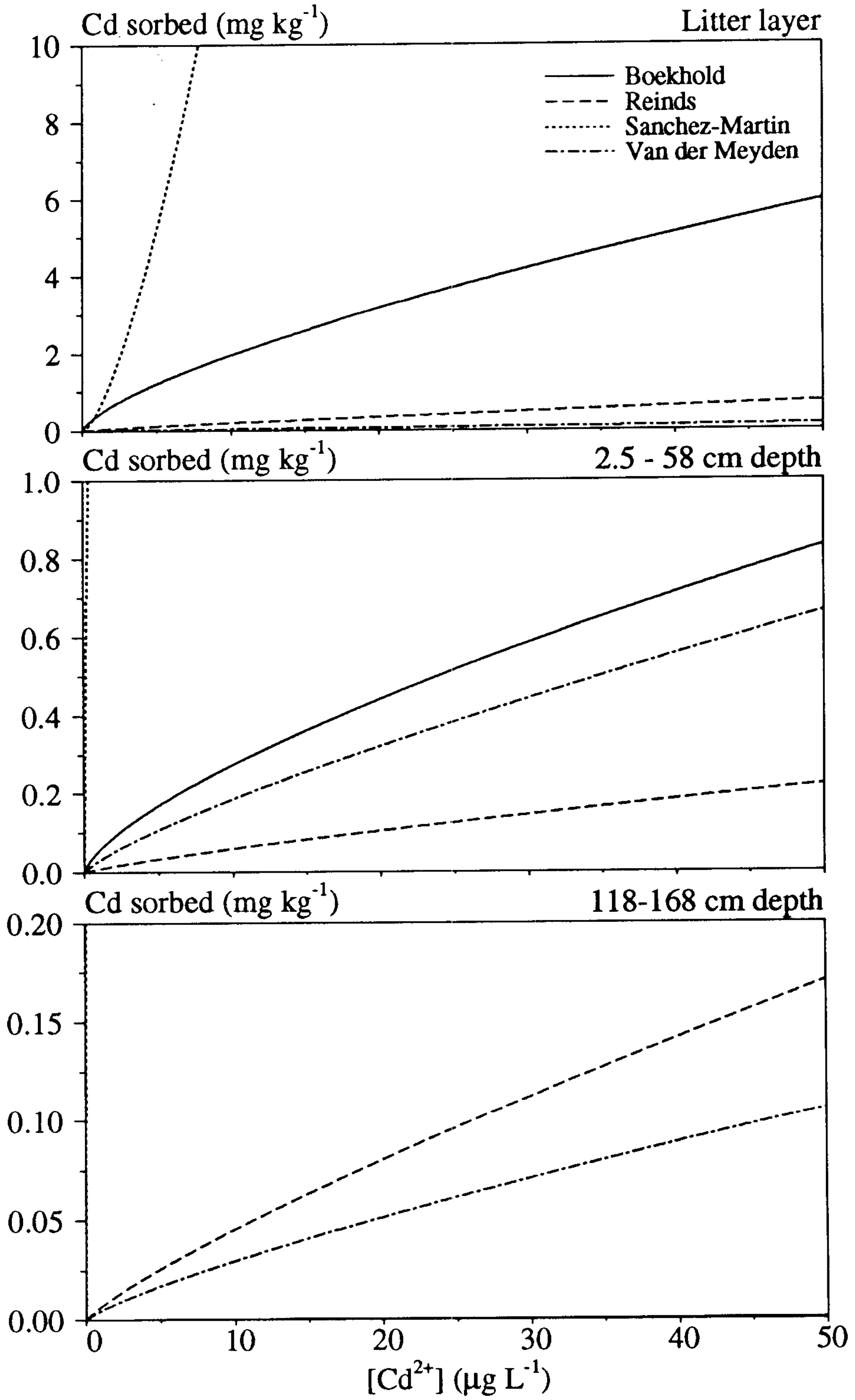


Figure 12 Comparison of Freundlich adsorption isotherms for Cd in soil reported by Boekhold (1992), Van der Meyden (1987), Sánchez-Martín and Sanchez-Camazano (1993), and Reijnds *et al.* (1995).

5.3 Results of the simulations

Eight simulations were run covering the uncertainties with respect to cadmium deposition, soil pH, sulphate deposition and cadmium adsorption behaviour discussed in §5.2 (TABLE 4). Results are summarized in TABLE 4 and compared with the observed cadmium accumulation in the litter layer and the observed free cadmium concentration in groundwater (i.e. the concentration at 4 m depth). For scenario's A, B, C and D it is important to note that for depths below 1.18 m the organic matter content was assumed to be zero. As a result there is no cadmium sorption below this depth.

TABLE 4
Results of the simulations (1988).

simulation	deposition of cadmium	deposition of sulphate	pH-value of the soil	Freundlich coefficient[a]	accumulation in litter. (mg kg^{-1})	Leachate at 4 m depth. (mol L^{-1})
Measured					1.7	$1.6\ 10^{-07}$
A	constant	constant	constant	0.051	0.69	$3.38\ 10^{-09}$
B	variable	constant	constant	0.051	0.48	$1.66\ 10^{-09}$
C	variable	variable	constant	0.051	0.47	$1.83\ 10^{-09}$
D	variable	variable	variable	0.051	0.40	$4.66\ 10^{-12}$
E	variable	variable	variable	0.051[b]	0.40	$0.00\ 10^{+00}$
F	variable	variable	variable	0.017	0.12	$2.40\ 10^{-08}$
G	variable	variable	variable	0.153	1.23	$0.00\ 10^{+00}$
H	variable[c]	variable	variable	0.051	1.82	$1.51\ 10^{-07}$

[a] for the mineral layer with an organic matter content of less then 0.1 %, the organic matter content is 0.00%, this means that there will be no sorption onto the soil matter

[b] for the mineral layer with an organic matter content of less then 0.1 %, the organic matter content is 0.05%

[c] ten times higher deposition of cadmium.

Scenario A

In this scenario, the deposition of Cd is assumed constant. As a result, the amount of adsorbed Cd in the litter layer gradually increases until a steady state is reached in 1930. Both the cadmium content in the litter layer, and the cadmium concentration in groundwater are strongly underestimated (TABLE 4). Cd breakthrough at 1 m depth starts around 1950. As the organic matter content below 1 m depth is zero, retardation of Cd below 1 m depth is negligible (Figure 14).

Scenario B

This scenario shows a peak in atmospheric Cd deposition between 1960 and 1975 (Figure 10). As a result, the predicted cadmium accumulation in litter also shows a peak. Furthermore, the simulated concentrations in 1988 are lower than for scenario A due to net desorption of Cd after 1973. In the same time, predicted groundwater concentrations are somewhat lower compared to scenario A. Breakthrough of Cd starts around 1960 (Figure 14). The retardation of the deposition peak is about 50 years.

Scenario C

This scenario shows a sulphate deposition peak between 1960 and 1970 (Figure 10), possibly causing enhanced mobilization and leaching of cadmium. The adjustment of the sulphate deposition trend has no effect on the total cadmium concentration in the litter layer. The predicted Cd concentration in the leachate at 4 m depth increases by 9% (TABLE 4). This minor increase is mainly caused by the increased mobility of Cd by sulphate complexation. As the total dissolved Cd concentration decreases with depth, and Cl^- and SO_4^{2-} behave as conservative tracers, the contribution of sulphate and Cl^- complexes to the total mobile concentration of Cd increases with depth. As Cl^- and SO_4^{2-} are conservative tracers, transport of Cl^- and SO_4^{2-} could have been neglected in this particular model application.

Scenario D

As none of the previous scenarios compare reasonably well with the observed concentrations, a scenario was analysed using time dependent pH values simulated with the model ReSAM (Figure 11). These pH values show a gradual decrease of pH until about 1975, followed by a stabilization or even a slight increase of the pH after this year. In general, these simulated pH values compare reasonably well with the 1988 pH-$CaCl_2$ values (TABLE 4). Lower pH values cause a decrease of the effective Freundlich sorption constant, resulting in less accumulation of Cd in the litter layer, and an increase of Cd leaching (Figure 14). Breakthrough of Cd at depths below 1 m starts around the year 2000. Simulated dissolved Cd concentrations are 4000 times lower than the observed concentrations in 1988. The distribution of adsorbed cadmium (Figure 13) shows that most cadmium is adsorbed in the upper 30 cm of the mineral soil.

Scenario E

In this scenario, the organic matter content of the subsoil is increased slightly (from 0 to 0.05%). This scenario was included to illustrate the enormous potential sorption capacity of the subsoil. In this scenario, breakthrough of Cd at 1 m depth starts in 2010. The total cadmium concentration in leachate is 10^{-3} µg L^{-1} in 2043 (Figure 15).

Scenario F

None of the previous scenarios led to model results coming close to the observations. Therefore, in this run the Freundlich adsorption constant was divided by three, which is within the range of uncertainty. The accumulation of Cd in the litter layer is reduced to about one eight of the observed value. The leachate concentration at 4 m, however, increases to one fifth of the observed value (TABLE 4). Breakthrough of Cd starts around 1920, and the maximum leachate concentration is reached around 1985 (Figure 15). Thus, the effective retardation is reduced to only 12 years. In contrast to scenario D, in scenario F substantial amounts of cadmium are sorbed between 0.3 and 1 m soil depth (Figure 13).

Scenario G

In this scenario, the sorption constant is increased by a factor 3. The accumulation of Cd in litter increases to 75% of the 1988 observed value, but no Cd is leached to the groundwater. About 30% of the total amount of Cd in the soil is present in the litter layer, while in scenario D this was about 10% (Figure 13).

Scenario H

The previous assumption for reconstructing the historic Cd deposition from the actual accumulation in litter and the Ah horizon (§5.2.2) is clearly falsified by the simulated distribution of adsorbed cadmium with depth for scenarios E through G. Taking scenario F as the most probable scenario, less than 10% of the cumulative Cd deposition is accumulated in the litter layer. In the same time, simulated soil contents below 2.5 cm depth are less than 0.1 mg kg^{-1}, which is below the detection limit. In other words, model calculations indicate that the major part of the deposited Cd is accumulated in the mineral soil at concentrations below the detection limit.

The final simulation was carried out with a tenfold increase of Cd deposition over the entire simulation period. This high deposition scenario is more in accordance with the estimates of accumulated Cd deposition based on regional procedures (§5.2.2). This scenario shows an almost perfect reconstruction of both the observed total Cd concentration in litter and the groundwater concentration. Most Cd (70%) is adsorbed in the mineral soil layers between 2.5 and 30 cm depth (Figure 13). Total Cd contents in these layers is about 0.50 mg kg$^{-1.}$ As this is above the detection limit, this is not in accordance with the observations. The total amount of Cd accumulated in litter and mineral soil in 1988 is 0.42 g m^{-2} while cumulative deposition was 0.51 g m^{-2}, meaning that 0.09 g m^{-2} (18%) of the total Cd input left the soil profile by leaching. The maximum Cd concentration at a depth of 4 m is reached around 1995, which is 22 years after occurrence of the Cd deposition peak in 1973 (Figure 15). The retardation of the Cd front below a depth of 1.18 m is negligible as there is no sorption capacity below this depth. Notice that the retardation of the Cd peak is less than for scenario D. An explanation can be found from the non-linearity of the Freundlich isotherm, which results in longer travel-times at low concentrations.

If we assume that scenario H is the most probable scenario, the retardation of about 22 years implies that in 'De Kempen' area groundwater pollution by Cd currently peaks. In the near future, the groundwater quality will only slowly improve. The simulation further suggests that the Cd concentrations in groundwater are almost independent of depth below 1 m depth. This gives a justification for using the arithmetic mean of the five observed groundwater observations for this model application.

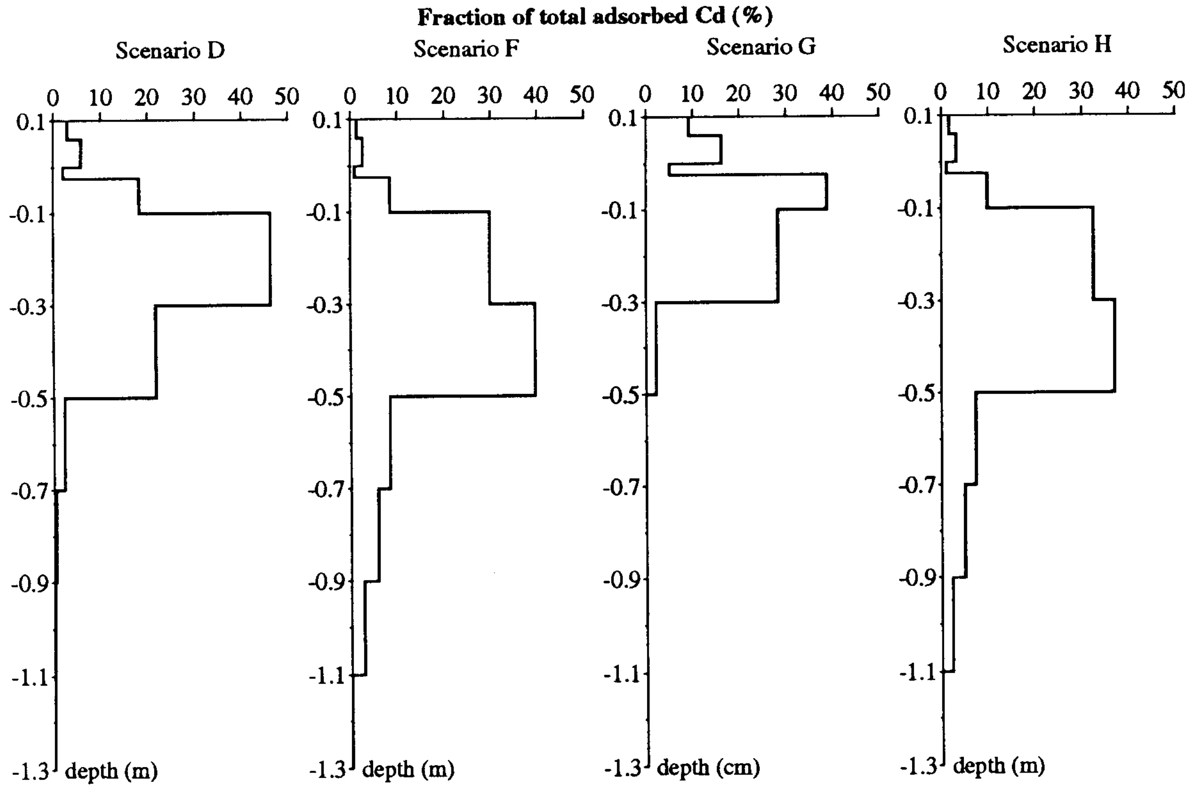


Figure 13 Distribution of total adsorbed Cd throughout the soil profile

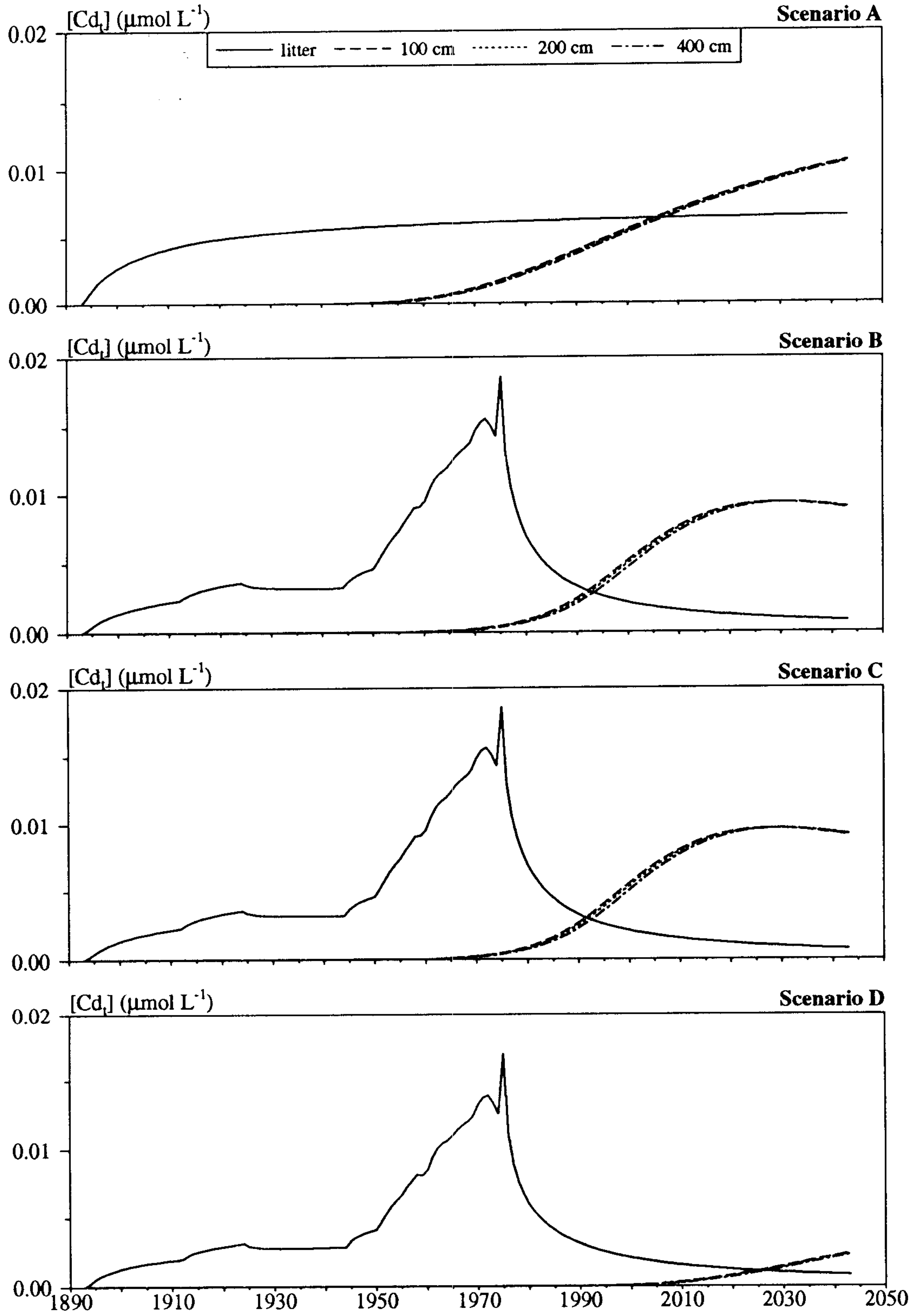


Figure 14 Simulated mobile Cd concentration for scenarios A-D. See text for explanation.

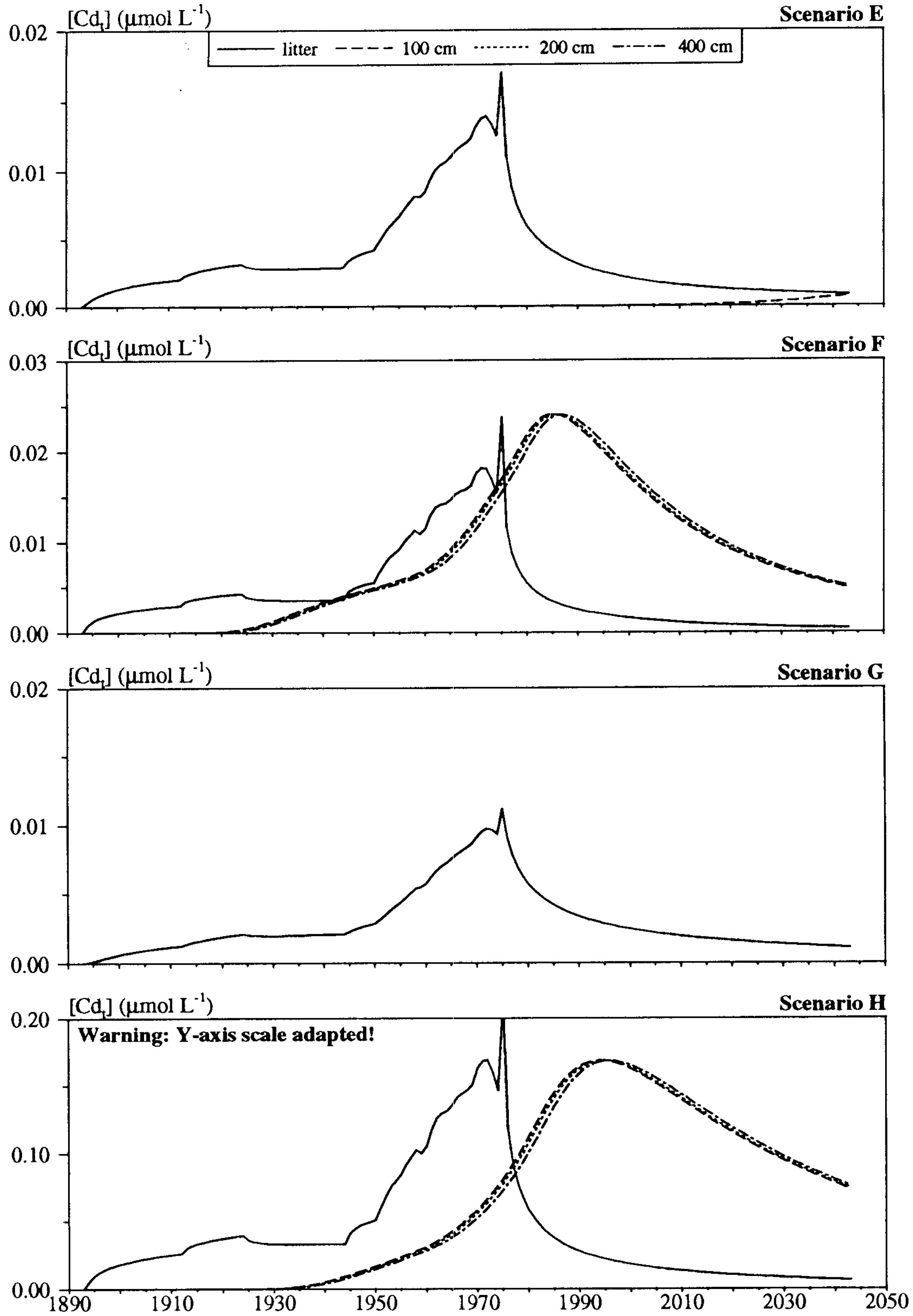


Figure 15 Simulated mobile Cd concentration for scenarios E-H. See text for explanation.

5.4 Conclusions

Although the application of METRAS to the Strijper Aa site, can by no means be considered a validation, the application has increased the confidence in the model concept and model parameterization and has improved our understanding of the variation of Cd accumulation with depth and time. The following major conclusions can be drawn:

- METRAS is technically applicable to assess transport and accumulation of Cd over time scales of decades to centuries for soil profiles of several meters thickness at (model) time resolutions down to one day and depth resolutions ranging from 5 to 40 cm. After optimization (see appendix B), the cpu time for a run of 150 years and 21 layers on a HP700 workstation is about 6 minutes. Most model parameters for METRAS can be derived from standard soil analyses (soil pH, organic matter content), standard experiments (adsorption isotherms) and textbooks (e.g. dispersion lengths).
- Adsorption of Cd could be described using one isotherm, derived for an arable field and adjusted for this application by correction for pH and organic matter content.
- Local data about atmospheric deposition are scarce and in general very uncertain. In general historical data about heavy metal inputs are not available and have to be reconstructed making additional and uncertain assumptions. For Cd deposition a relation was assumed between deposition and metal production at the smelter.
- For historic pH, independently obtained output data from the soil acidification model RESAM were used, which, for 1988, were lower than observed values pH-H_2O values but comparable to pH-$CaCl_2$ data.
- The total amount of Cd accumulation in the soil can not be estimated from summing the observed total Cd concentration because most Cd is accumulated in the mineral soil at concentrations below the detection limit. Accumulation of Cd in soil layers with negligible organic matter contents can be very substantial. When assuming finite, but analytically undetectable, organic matter contents, METRAS predicts no breakthrough of Cd at present. When assuming zero organic matter contents for soil layers with organic matter content below the detection limit, there is no further retardation of the Cd front below this depth.
- METRAS can be parameterized in a realistic way such that both accumulation in litter and concentrations in groundwater agree with observations of respectively 1.7 mg kg^{-1} and 0.16 μmol L^{-1}. However, the range for accumulation in litter is 0.12-1.82 mg kg^{-1} and for groundwater concentrations 0-0.151 μmol L^{-1}, for equally realistic parameterizations of METRAS.
- METRAS predicts that Cd concentrations in litter will quickly decrease in the coming years, while the groundwater concentration will further increase and remain high for several decades. These results may be helpful to develop monitoring strategies.
- No proof was found that effects of Cd-complexation by DOC and macro-dispersion, which were not considered in METRAS, were relevant for modelling Strijper Aa.

6 REMARKS AND RECOMMENDATIONS

At present the METRAS model has only been applied at one site (a forest site in the Strijper Aa area), and has only been parameterized for cadmium. Although this application can by no means be considered a validation study, it has improved the confidence in the model concept and model parameterization, and has improved our understanding of the behaviour of cadmium in the soil system. It can be concluded that as an intended standard tool for the Environmental Outlook to predict concentrations in the upper groundwater:

- there are no major technical or logistic problems to apply METRAS at a national scale, making use of experiences with PESTRAS (Tiktak *et. al.*, 1995). Within 24 h a total of about 360 cases can be evaluated over a period of 100 years. (taking into account optimization of numerical procedures described in Appendix B).
- collection of equilibrium constants of METRAS and development of reaction submodels for other metals than Cd is not expected to give new problems and therefore can be carried out rather fast by an experienced soil chemist.
- most METRAS parameters that vary regionally, with location (weather), soil type (adsorption parameters, solute transport parameters) can be derived from standard data sets (soil pH, organic matter content), standard experiments (adsorption isotherms) and textbooks (dispersion lengths).
- historical data about heavy metal inputs and soil conditions are not available or highly uncertain and can only be derived by expert judgement or by retrospective modelling (pH).

The provisional model application study has also shown that leaching of heavy metals to the groundwater is a real problem which may become even more serious in the coming decades.

Still there are various topics that have to be dealt with before METRAS can be applied reliably for all relevant metals (Cd, Cu, Pb, Zn, Ni, Cr, Hg and As):

- mobilization of natural organic ligands and subsequent complexation with metals. Although this process is rather unimportant for Cd, it will be important for at least Cu and Pb.
- macro dispersion (see eg. van der Zee and van Riemsdijk, 1987) was not considered and is expected to have considerable effect on the average leaching behaviour.
- hysteresis of the adsorption process is not considered and may lead to an overestimation of metal leaching.
- application of METRAS for arable soils where fertilizer and manure are the major sources of Cd, and pH values are near neutral. Complexation behaviour in these systems will be different from that in forest soils.
- the importance of short term variations of temperature, pH, DOC, water flow on the behaviour of heavy metals is not yet quantitatively evaluated,

- comparison of results of METRAS with those of simple box-models, like eg. SOACAS (Vissenberg and van Grinsven, 1995) with respect to predicted metal accumulation in the top soil. Data requirement and run times for box models are smaller than for multi-layer models like METRAS, but box-models are only suitable to predict accumulation in the topsoil, and not to calculate leaching to groundwater

In spite of all these unresolved problems METRAS may become a useful tool to predict metal accumulation and leaching, both on a regional scale and on a local scale, and particularly for scenarios where land-use is changed.

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APPENDIX A List of definitions

Adsorption

Adherence of the atoms, ions, or molecules of a gas or liquid to the surface of another substance, called the adsorbent.

Component

Mathematically, these are the independent variables of the mass balance equations. They are chemical entities that are used to create every species via a chemical reaction involving these entities.

Compound

A substance composed of atoms or ions of two or more elements in chemical combination. The constituents are united by bonds of valence forces. A compound, a homogeneous entity where the elements have definite proportions by weight and are represented by a chemical formula. A compound has characteristic properties quite different from those of its constituent elements.

Complex compound

A compound formed by the union of a metal ion with a nonmetallic ion or molecule.

Precipitate

Small particles that have settled out of a liquid or a gaseous suspension by gravity, or that result from a chemical reaction.

Species

Chemical entities that are the result of reactions in which the reactants are components. There are two kinds of species soluble species and solids.

Soluble species

Any species that can exist in the aqueous phase. A soluble species can be a soluble component or a complex (i.e., the product of chemical reactions involving components). They can include aqueous species (e.g., Cd^{2+}, H^+, SO_4^{2-}), complexes (e.g., $CdC0_{3(aq)}$), etc.
The concentration of all soluble species is variable and is a function of the species' thermodynamic data and the concentration of the components that compose the species.

Solids

Any species that have a fixed activity. For regular solid phases (e.g., $CaC0_{3(s)}$, $Al(OH)_{3(s)}$) the activity is equal to one. There are two kinds of solids: precipitated and dissolved.

Precipitated solids

Solids that have the potential to dissolve if their solubility constraints are not met. If solubility constraints are not met, (i.e., the system is undersaturated) the solid will be converted to a dissolved solid and included into the calculation. Precipitated solids have a fixed activity.

Dissolved solids

Solids that have the potential to precipitate if their solubility constraints are exceeded.

APPENDIX B Optimization of the mass balance equation

This appendix describes a study on the computation of chemical equilibria for the modelling of cadmium in soil. METRAS uses a standard Newton-Raphson procedure to calculate the concentration of the free heavy metal ion. Two topics are handled in this appendix: firstly, the derivation of the mass balance equation as a function of the free ion concentration and secondly the implementation and testing of a more efficient Newton-Raphson procedure to solve this mass balance equation.

B.1 Chemical equilibria

The equations used in the cadmium model are derived here for a more general case of a compound Z, which consists of two species X and Y:

$$Z \rightleftharpoons \alpha X + \beta Y. \tag{B1}$$

For each species S we define a concentration [S] and an activity (S) which are related by the activity constant f_S:

$$(S) = f_S[S]. \tag{B2}$$

The equilibrium constant K_Z is defined as:

$$K_Z = \frac{(Z)}{(X)^{\alpha}(Y)^{\beta}}. \tag{B3}$$

Using the abbreviations

$$a = K_Z f_X^{\alpha} f_Y^{\beta},\ b = [Y_{tot}],\ c = f_Z, \tag{B4}$$

we can derive from (B2) and (B3):

$$c[Z] = a[X]^{\alpha}[Y]^{\beta}, \tag{B5}$$

from which follows:

$$[Y] = \left(\frac{c[Z]}{a[X]^{\alpha}}\right)^{\frac{1}{\beta}}. \tag{B6}$$

Substituting this in the mass balance equation for species Y

$$[Y_{tot}] = [Y] + \beta[Z], \tag{B7}$$

we get:

$$\beta[Z] + \left(\frac{c[Z]}{a[X]^{\alpha}}\right)^{\frac{1}{\beta}} - b = 0. \tag{B8}$$

If X is the species we are concerned with (for instance cadmium), a solution of (B8) has to be found for [Z] as a function of [X]. For the values α = 1,2 and β = 1,2 equation (B8) can be solved explicitly (see §B.6) for solutions).

If a carbonate is involved, then the equations for the concentration of this carbonate are somewhat different; it is assumed that the CO_2 pressure and pH in the soil are conditions imposed on the soil system. In this case the equilibrium constant for the equilibrium

$$CO_{2\,gas} + H_2O \rightleftharpoons 2H^+ + CO_3^{2-},\ \text{is}\ K_{p_{CO_2}} = \frac{p_{CO_2}}{(H^+)^2(CO_3^{2-})}. \tag{B9}$$

From this, the CO_3^{2-} concentration can be solved immediately and substituted into the equilibrium constant for the carbonate:

$$XCO_3 \rightleftharpoons \theta X + \delta CO_3^{2-},\ K_{XCO_3} = \frac{(XCO_3)}{(X)^{\theta}(CO_3^{2-})^{\delta}}. \tag{B10}$$

As a result we get:

$$[XCO_3] = \frac{K_{XCO_3}}{f_{XCO_3}}\{f_X[X]\}^{\theta}\left(\frac{p_{CO_2}}{\{f_{H^+}[H^+]\}^2 K_{p_{CO_2}}}\right)^{\delta}. \tag{B11}$$

Adsorption to the soil is described with an extended Freundlich equation:

$$[X_{sor}] = K_{eff}(X)^n(H^+)^m. \tag{B12}$$

with K_{eff}, n and m Freundlich parameters (n, m non-integer).

Finally, the mass balance for X has to be solved:

$$[X_{tot}] = [X] + \alpha[Z] + [XCO_3] + [X_{sor}]. \tag{B13}$$

This equation, in which [Z] (see §B.6) and equations (B11) and (B12) have to be substituted, is a one-dimensional, non-linear equation for the concentration [X]. Note that more terms of the type α[Z] can be present for different compounds in this mass balance equation.

B.2 Solution procedure

The mass balance equation for X, can be solved with any routine which can find a zero of a function. Since, in a dynamical model, equilibria have to be calculated very often, it is desirable that the method is efficient. The Newton-Raphson method is known for its efficiency, but can however give difficulties if a start value is provided which is not close enough to the solution of the problem. Another difficulty might be the expensive calculation of the required derivative of the function. However, in this case the derivative is explicitly known (see §B.6 for the derivative of [Z]) and rather easy to compute.

In the current implementation of the Newton-Raphson procedure in the METRAS model, use has been made of the RTSAFE routine of Numerical Recipes (Press *et al.* 1986). RTSAFE combines the Newton-Raphson method with a bisection method. A lower bound and a higher bound have to be provided between which the zero to be found must lie. RTSAFE adapts these lower and higher bound during the iteration process. Newton-Raphson is used unless one of the following two conditions forces RTSAFE to use bisection:

- the next Newton-Raphson iterate does not lie inside the interval defined by the lower and higher bound (derivative small)
- the next Newton-Raphson iterate lies too close to the current one (derivative large).

In some preliminary tests on equilibria computations for cadmium, serious drawbacks to this routine became apparent:

- the initial guess for the Newton procedure is taken as the midpoint of the lower, higher bound interval. No 'educated guess' of the solution, for instance the concentration at the previous time step, can be put into RTSAFE.
- the switch to bisection and the adaptation of the lower, higher bound is programmed in such a way that even for a linear function 21 steps were needed for an accuracy of 7 digits; normal Newton-Raphson would need one step only. This will not only occur for a linear function, but it also happened often during our equilibria computations. It appears that if a function value zero has been found, the program always switches to the bisection method.
- convergence is reached if the absolute difference between the two last iterates drops below a user defined absolute accuracy. In a typical example of a breakthrough process in a column of soil, there are several orders of magnitude difference in concentration, both in time as in depth. If very low concentrations have to be predicted accurately, a very low absolute accuracy is needed, implying too accurate and expensive results for high concentrations.

A new version of RTSAFE has been implemented, which has the following features:

- input of an 'educated guess' as initial value for the Newton iteration; for equilibria computations the following options are available:
  1 midway between lower bound, higher bound
  2 concentration at old time step
  3 concentration assuming total adsorption (see below, equation (B16))
  4 $[X_{tot}]$
  5 $([X]_{t-1} / [X_{tot}]_{t-1}) [X_{tot}]_t$, assuming a constant ratio $[X]/[X_{tot}]$
- a check if the function value has become zero
- a mixed absolute, relative accuracy in the convergence test; the absolute accuracy is used for very low concentrations, the relative one is used for high concentrations; for two iterates $x^{(i)}$ and $x^{(i+1)}$ the convergence criterion is:

  $$|x^{i+1}-x^{i}| < \max(\varepsilon_a, \varepsilon_r |x^{i+1}|), \qquad \text{(B14)}$$

  with ε_a an absolute accuracy and ε_r a relative accuracy.

Furthermore, some special properties of the mass balance equation for X have been taken into account. The function $f([X]) = [X_{tot}] - \{ [X] + \alpha[Z] + [XCO_3] + [X_{sor}] \}$ is a strictly decreasing function of [X], with an infinite derivative for [X] = 0.

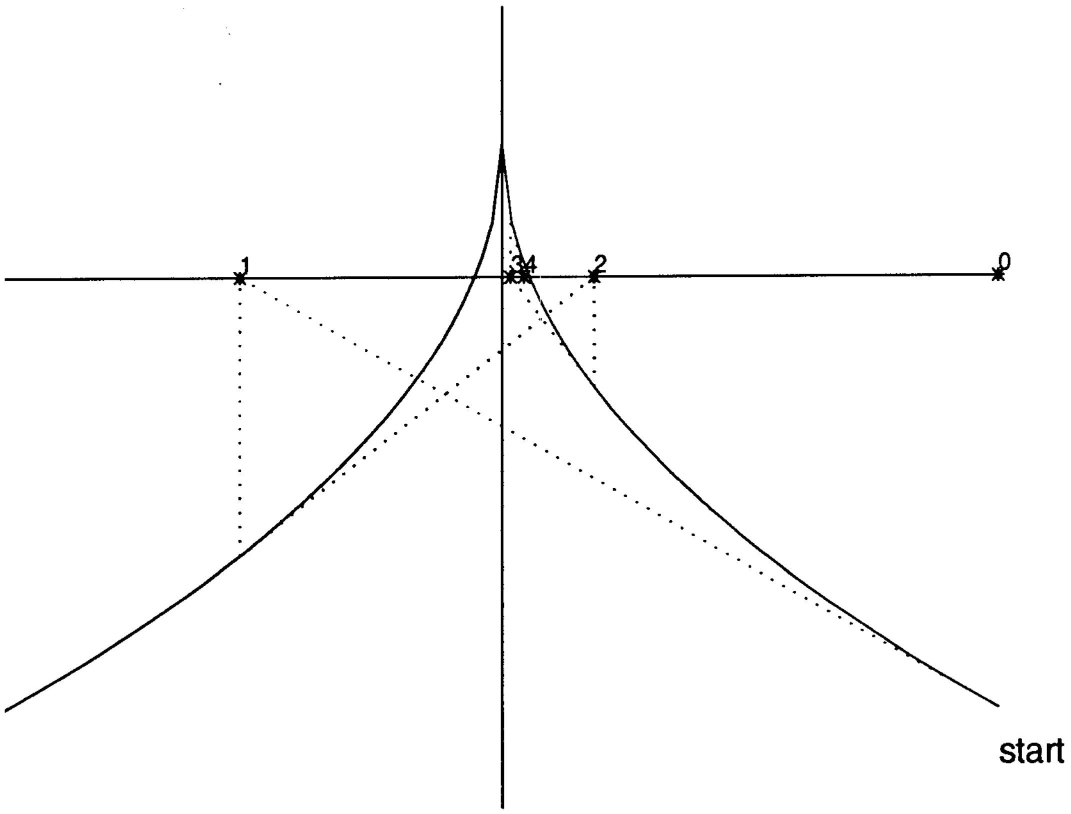

Figure B1 Newton-Raphson process for symmetrically extended mass balance function.

Precautions have been taken not to start in [X] = 0 with the Newton-Raphson process. If the initial value for the iteration should be zero (for instance zero concentration in the previous time step), then it is assumed that all of the species X is adsorbed to the soil, reducing the mass balance equation to

$$[X_{tot}] = [X_{sor}] = K_{eff}(X)^n (H^+)^m, \tag{B15}$$

giving a new initial guess

$$[X] = \frac{1}{f_x}\left(\frac{[X_{tot}]}{K_{eff}\{f_{H^+}[H^+]\}^m}\right)^{\frac{1}{n}}. \tag{B16}$$

If the initial guess for Newton-Raphson is too far to the right, the next iterate may well become negative. Since this would cause RTSAFE to switch to the slower bisection process, the above function was symmetrically extended for negative values. In this way the next step is again a Newton step (see Figure B1).

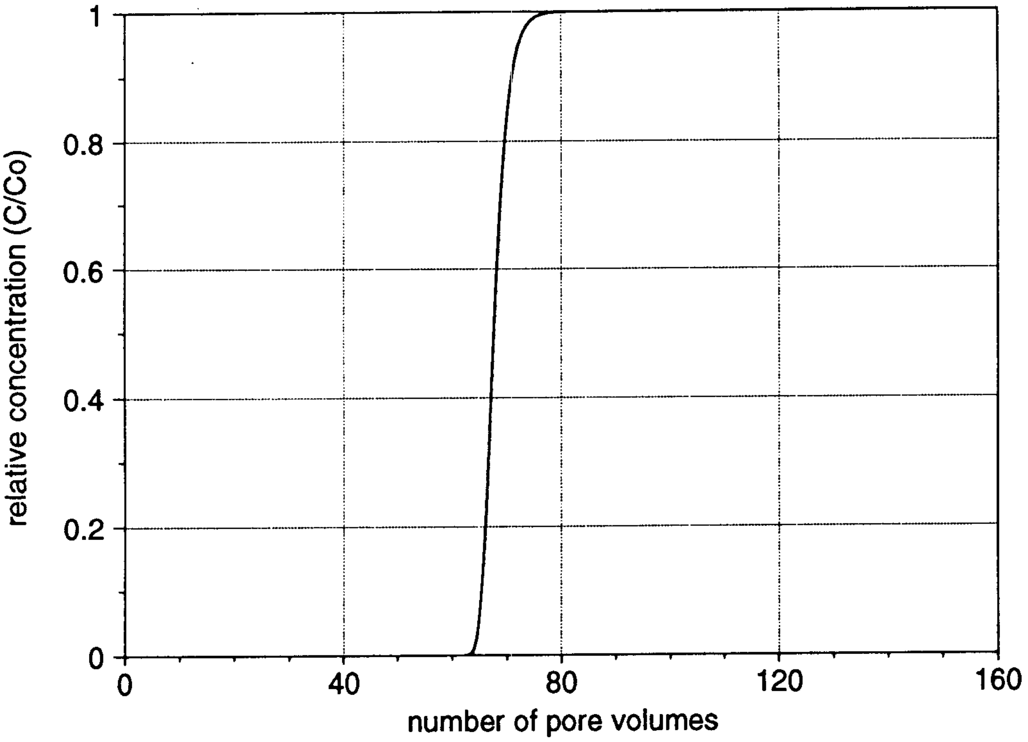

Figure B2 Results of test 1.

The computation of the function *f* and its derivative have been implemented more efficiently using the formulas in §B.6.

Note that all above remarks and program alterations have only been tested for $\alpha = 1$ and $\beta = 1$ (cadmium). We think they are also valid for other values of α,β but this would need some thought.

B.3 Test results

Two tests problems have been simulated to test the new version of the Newton-Raphson routine. Different versions of the program were used:

version 0:	original version
version 3:	version with new features RTSAFE and more efficient implementation of function evaluation and derivative
version 4:	as 3, with extra check for constant [Cd_{tot}]. For some simple cases (a.o. temperature and pH constant in time), the Cd concentration [Cd^{2+}] does not change if the total Cd concentration [Cd_{tot}] is the same as in the previous time step. A simple check has been implemented whether [Cd_{tot}] remains constant in which case RTSAFE does not have to be called.

version 5: as 4, but instead of RTSAFE the zero finder ZEROIN (Bus and Dekker, 1975) has been used.

The first test used a very simple flow regime (constant downward flow), constant temperature and a homogeneous soil. The species involved are Cd^{2+}, Cl^-, SO_4^{2-}, $CdCl^+$, $CdSO_4$, $CdCO_3$ and cadmium adsorbed to soil. Different runs were done, using different values for the starting value of the Newton-Raphson process and for the absolute and relative accuracies. Calculations were done using a specific test version for EQCAD, the computer program which computes equilibria for cadmium, which used a fixed time step. The main conclusions that can be drawn from the test runs are:

- nearly all versions succeeded in representing the breakthrough curve of the original version (Figure B3) correctly; the difference in the normalized concentration stays below $5 \cdot 10^{-3}$ (see Figure B4 for a comparison of the results of run with version 4, start option 2, absolute accuracy 10^{-18}, relative accuracy of 10^{-2} with the original version, absolute accuracy 10^{-22}). Only version 5 with large accuracies did not reproduce the correct results (for an explanation see below).

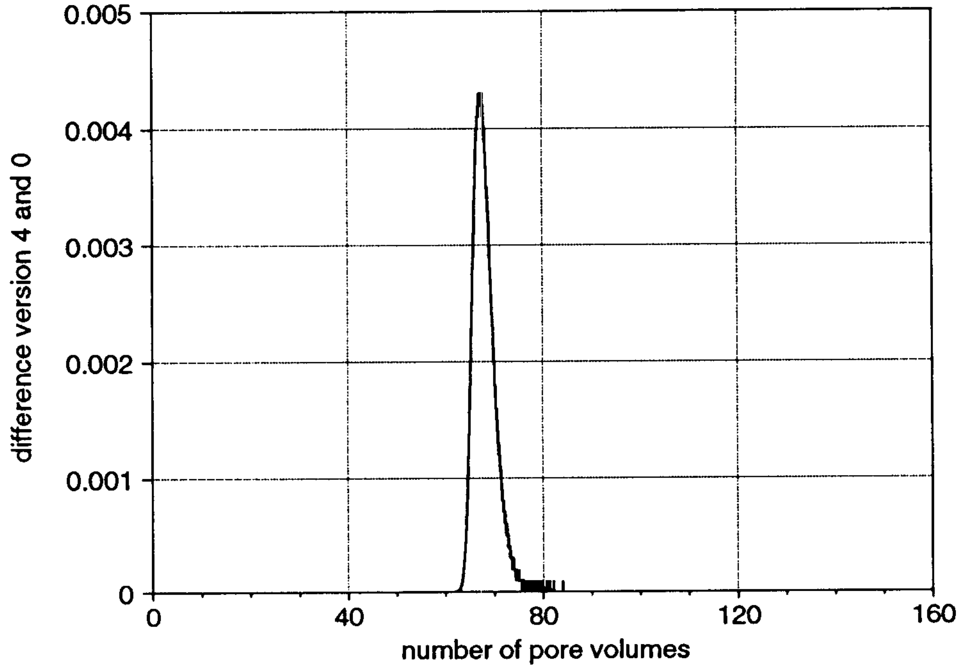

Figure B3 Difference between version 4 and the original version.

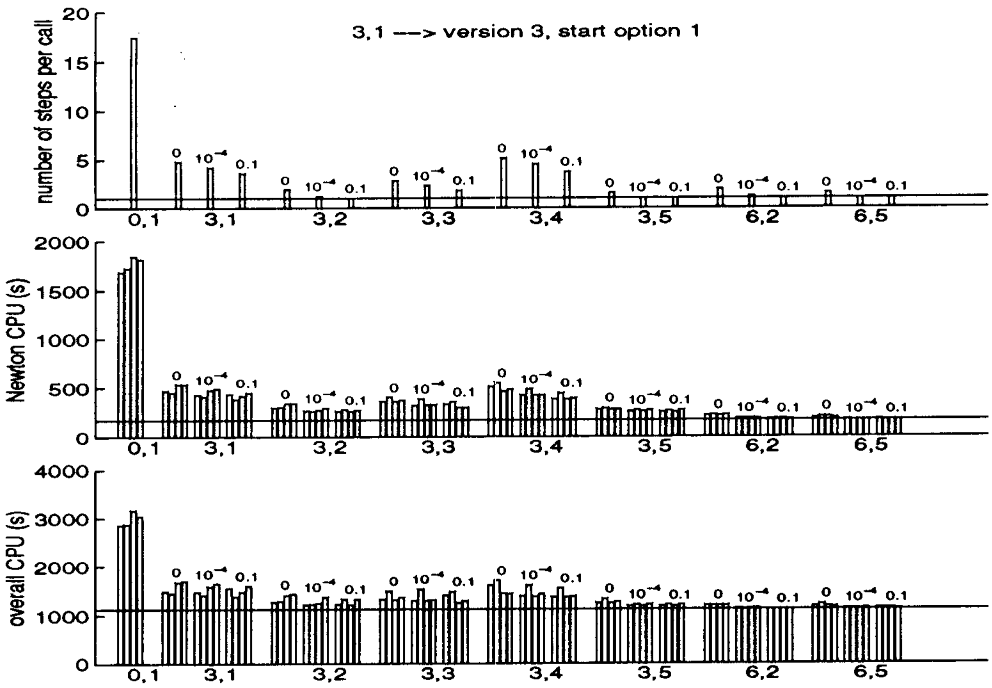

Figure B4 Timings test 2 for different versions and relative accuracies of 0, 10^{-4} and 0.1.

- No bisection steps are needed any more.
- Version 4 is the fastest version. However, in more general cases the assumptions (e.g. constant temperature, constant pH) from which we may conclude that [Cd^{2+}] remains constant may not hold.
- For version 3, start option 2 (using the concentration at the previous time step) and start option 5 (assuming a constant ratio [Cd^{2+}]/[Cd_{tot}]) are the best choices. Option 2 is a bit faster for this test case.
- The average number of iteration steps per RTSAFE call drops from 21 (original version) to 0.34 (version 3, option 2). It seems strange that this number drops below one, but this indicates that many RTSAFE calls are not needed since the start value is already correct. This is because very often "nothing happens", due to constant parameters and constant [Cd_{tot}]. In version 4 we see that, avoiding RTSAFE calls when nothing happens, the average number of iteration steps goes to 1.1.
- The CPU time for the Newton-Raphson process (including function and derivative evaluation and choosing an appropriate starting value) shows a speed-up factor of 7 between the original version and version 3, option 2. Overall CPU time has decreased with a factor 2.8. For the specific version 4 speed ups are approx. 25 (Newton) and 10 (overall).
- The amount of work involved in the Newton-Raphson procedure drops from 70 % (original version) to 30 % (version 3, option 2). This means that for further speed-up also other parts of the program have to be looked at.
- The speed up due to larger values of relative accuracy is not so large. Comparing a relative accuracy of 0 and 0.01 (version 3, option 2) shows that the average number of iterations per

call halves, but the CPU time only drops by 15 %. Obviously a lot of overhead is done, partly due to the fact that only very few iteration steps (1 or 2) are taken in most cases.

- version 5 (using ZEROIN) is not reliable for larger values of the relative accuracy, probably due to the different usage of accuracy in ZEROIN and RTSAFE. In RTSAFE convergence is checked by comparing the difference between the two last iterates against the accuracy. ZEROIN gives two output values (lower and higher bound) whose difference is less than the accuracy and have in between a zero function value. For small values of the accuracy, ZEROIN is rather fast but can not match the pure Newton-Raphson method (so without the bisection steps of RTSAFE). For a general zero finder however, it is much better than the original RTSAFE routine.

A second test used the computer program METRAS, into which EQCAD has been implemented. It is a simulation of a case study of Cd transport in 'De Kempen'; simulation time is 150 year and the water flow is assumed to be constant. Since in this case the pH is not constant in time, version 4 and 5 could not be used.

A new version (version 6) has been used: it is the same as version 3, but without an initial test in RTSAFE whether there is a zero present in the interval [lower bound,higher bound]. In the cadmium equilibrium case we know that there must be a zero, so this expensive test (involving two function evaluations) can be left out.

The number of iterations per call to RTSAFE and timings of four sets of runs on a SUN Sparc 10 for different versions, different start options and three relative accuracies (0, 10^{-4}, 0.1) are shown in Figure B5. The absolute accuracy was 10^{-22} for version 0 and 10^{-18} for the other versions. The line drawn in the plots shows the minimal value (number of steps, CPU time). Note that the four sets only differ in CPU time; the runs are equal but the timing procedure (gprof) produces somewhat different results.

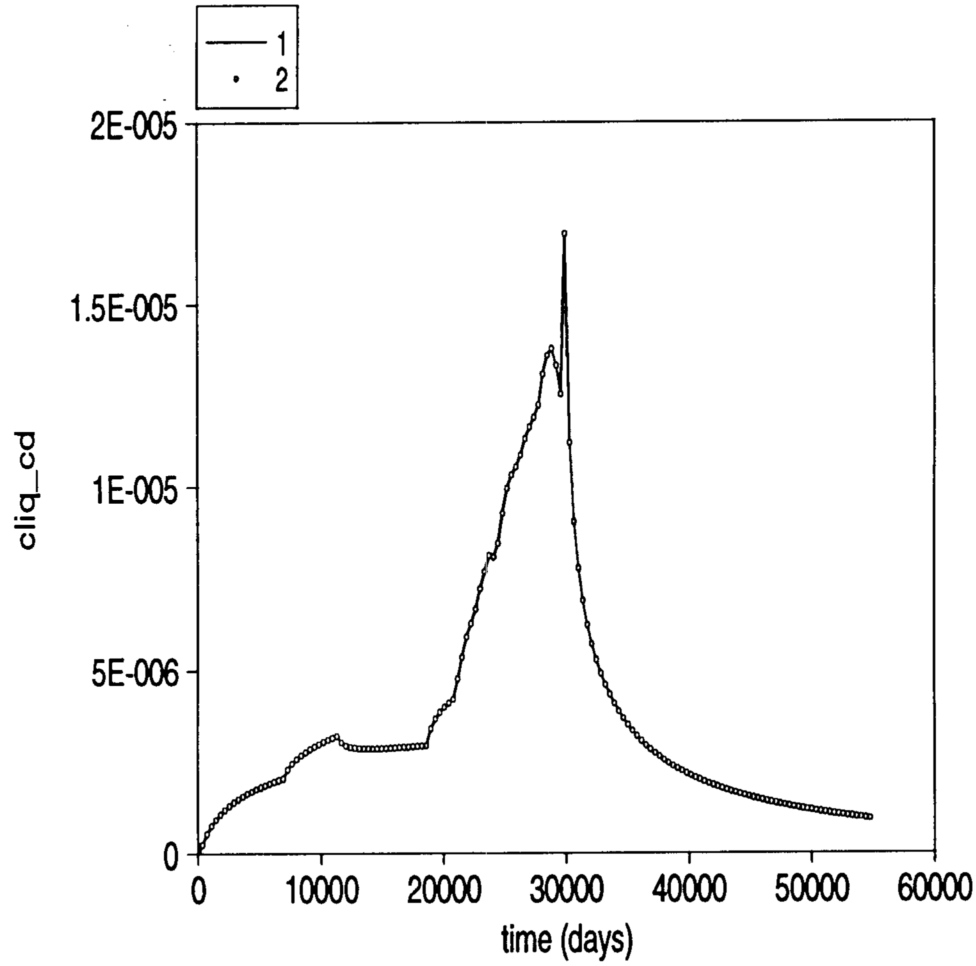

Figure B5 Cadmium concentration test 2. 1 refers to the original version, and 2 is version 6 with option 2 and relative accuracy of 0.01.

The main conclusions from this test case confirm the findings of test case 1.

- A relative accuracy of 0.1 was sufficient to get a reliable calculation of the cadmium concentration (see Figure B5). Apparently, time steps are so small that the initial value of the Newton process is very close to the concentration in the next time step and only one step of Newton-Raphson produces a much more accurate result as the predefined accuracy 0.1.
- Start options 2 (previous concentration) and 5 (assuming a constant ratio $[Cd^{2+}]/[Cd_{tot}]$) are the best choices.
- The average number of iteration steps per RTSAFE call drops from 17 (original version) to 1 (version 6, options 2 and 5).
- Using the new version 6, speed-up factors are 10 (Newton and related functions) and 2.7 (overall CPU) for option 5 compared with the original version.
- The amount of work involved for Newton-Raphson drops from 60 % (original version) to 15 % (version 6, option 5). This means that for further speed-up also other parts of the

program have to be looked at. Maybe the time stepping scheme could be improved using an implicit time stepping procedure. Now 130000 time steps are used for a simulation time of 150 years, an average of 2 time steps per day.

B.4 Conclusions and recommendations

The derivation of one mass balance equation in which chemical equilibria of several compounds are involved has been presented for a rather general set of equilibria. The mass balance equation is a function of the free ion of one species. This function (and its derivative) are now presented in such a way that they can be easily transformed into a FORTRAN code (see equations (B11), (B12), (B13) and §B.6). This has led to a more efficient FORTRAN implementation of the mass balance function.

A Newton-Raphson procedure to solve a mass balance equation for chemical equilibria has been implemented and has been tested for a cadmium model. The new version is 10 times as fast as the original Newton Raphson procedure (RTSAFE, Numerical Recipes), giving a speed up for the whole model of nearly 3.

Further speed up of the model can not be found in the Newton-Raphson procedure, since now it only takes 15 % of total CPU time. An implicit time stepping procedure may lead to a faster model. More efficient programming (e.g. taking computations out of a loop) may also be possible; examination of the source code and the time profiles is then necessary.

B.5 References

J.C.P. Bus, & T.J. Dekker, 1975. Two Efficient Algorithms with Guaranteed Convergence for Finding a Zero of a Function, ACM Transactions on Mathematical Software, 1:330-345(4).

MAPLE, 1994. Language for symbolic mathematical calculation, Waterloo MAPLE software, Univ. of Waterloo.

W.H. Press, B.P. Flannery, S.A. Teukolsky, & W.I. Vetterling, 1986. Numerical Recipes, Cambridge University Press, Cambridge.

B.6 Concentration of a compound as a function of the free ion concentration

Compound Z, $Z \rightleftharpoons \alpha X + \beta Y$.

Note: in the following capital letters are used to denote concentration ([ ] are left out).

$$a = K_Z f_X^{\alpha} f_Y^{\beta},\ b = Y_{tot},\ c = f_Z$$

Mass balance: $\beta Z + \left(\frac{cZ}{aX^{\alpha}} \right)^{\frac{1}{\beta}} - b = 0$

$$\beta = 1, Z = \frac{b a X^{\alpha}}{a X^{\alpha} + c}, \frac{dZ}{dX} = \frac{b a X^{\alpha} \alpha c}{(a X^{\alpha} + c)^2 X}$$

$$\beta = 1, \alpha = 1, Z = \frac{b a X}{a X + c}, \frac{dZ}{dX} = \frac{b a c}{(a X + c)^2}$$

$$\beta = 1, \alpha = 2, Z = \frac{b a X^2}{a X^2 + c}, \frac{dZ}{dX} = 2 \frac{b a X c}{(a X^2 + c)^2}$$

$$\beta = 2, Z = \frac{1}{16} \frac{\left(\sqrt{c}\sqrt{a}\, X^{(-1/2\,\alpha)} - \sqrt{a(c X^{(-\alpha)} + 8 b a)}\right)^2}{a^2}$$

$$\beta = 2, \frac{dZ}{dX} = \frac{1}{8} \frac{\alpha \left(-c a \sqrt{X^{\alpha}} \sqrt{\frac{a(c + 8 a b X^{\alpha})}{X^{\alpha}}} + c^{3/2} a^{3/2} + 4\sqrt{c}\, a^{5/2} b X^{\alpha}\right)}{a^2 X (X^{\alpha})^{3/2} \frac{\sqrt{a(c + 8 a b X^{\alpha})}}{X^{\alpha}}}$$

$$\beta = 2, \alpha = 1, Z = \frac{1}{16} \frac{\left(\sqrt{c} - \sqrt{c + 8 b a X}\right)^2}{a X}$$

$$\beta = 2, \alpha = 1, \frac{dZ}{dX} = -\frac{1}{16} \frac{\left(\sqrt{c} - \sqrt{c + 8 b a X}\right)\left(\sqrt{c}\sqrt{c + 8 b a X} - c\right)}{X^2 a \sqrt{c + 8 b a X}}$$

$$\beta = 2, \alpha = 2, Z = \frac{1}{16} \frac{\left(\sqrt{c} - \sqrt{c + 8\,b\,a\,X^2}\right)^2}{aX^2}$$

$$\beta = 2, \alpha = 2, \frac{dZ}{dX} = \frac{1}{8} \frac{\left(\sqrt{c} - \sqrt{c + 8\,b\,a\,X^2}\right)\left(-\sqrt{c}\,\sqrt{c + 8\,b\,a\,X^2} + c\right)}{a\sqrt{c + 8\,b\,a\,X^2}\;X^3}$$

APPENDIX C Derivation of the dispersion length

A simple and rough method is used to derive the dispersion length. For this derivation experimental data of Boekhold (1992) were used. A soil column is percolated with a constant flow, and a tracer is added at a known concentration. At the bottom of the column the tracer concentration in the solution is measured continuously. The results are graphically presented as a breakthrough curve; the relative concentration, c/c_o, is plotted against time (c is soil solution concentration, and c_o is concentration in the tracer solution). At t_m, the time when the concentration in percolate is half it's original concentration, a tangent line is drawn to the breakthrough curve. The distance between the intersection of the tangent line with the time-axis, and t_m is denoted as Δt. By applying the following equation the dispersion length can be obtained:

$$\alpha_L = \frac{\Delta t^2}{\pi t_m^2} L \qquad \text{(C1)}$$

where α_L (m) is dispersion lenght, L (m) is column length, t_m (s) is time at which the relative concentration in percolate is 0.5, and Δt is distance between the intersection of the tangent line and the time-axis. In the experiment results are expressed in dimensions of pore volumes:

$$PV = \frac{q\, t}{\theta\, L} \qquad \text{(C2)}$$

where PV (-) is pore volume, t (s) is time after application of the tracer, θ ($m^3\ m^{-3}$) is volumetric water content, and L (m) is column length.

Figure C1 shows the breakthrough curve for chloride as presented by Boekhold (1992). The experiment was carried out with a column of length L is 0.11 m, and a soil water flux of 1 m d^{-1}. The soil water content of the soil, θ, was 0.41 $m^3\ m^{-3}$. The values of Δt and t_m can directly be read from Figure C1. Δt was estimated at 0.20 pore volume, and t_m was 0.92 pore volume. Using these figures and eqn. (C1), a dispersion length, α_L, of 0.002 m was calculated.

Using these experimental data, a METRAS run was carried out for validation of the transport part of the model. Results are presented in Figure C2. The agreement between the observed and measured breakthrough curves is good, confirming the validity of the transport model for this particular application (i.e. sandy soil). However, the experimental data point at the importance of preferential flow, as t_m is somewhat smaller than 1. In case of convection-dispersion, t_m should be 1. The importance of preferential flow as a transport mechanism should be further analyzed.

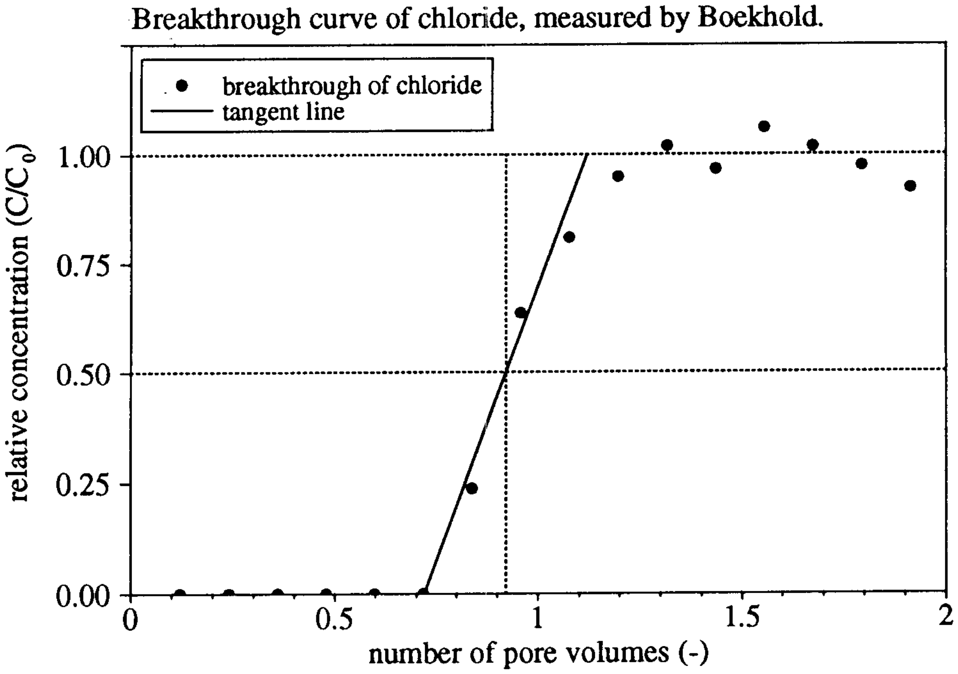

Figure C1 Derivation of the dispersion length.

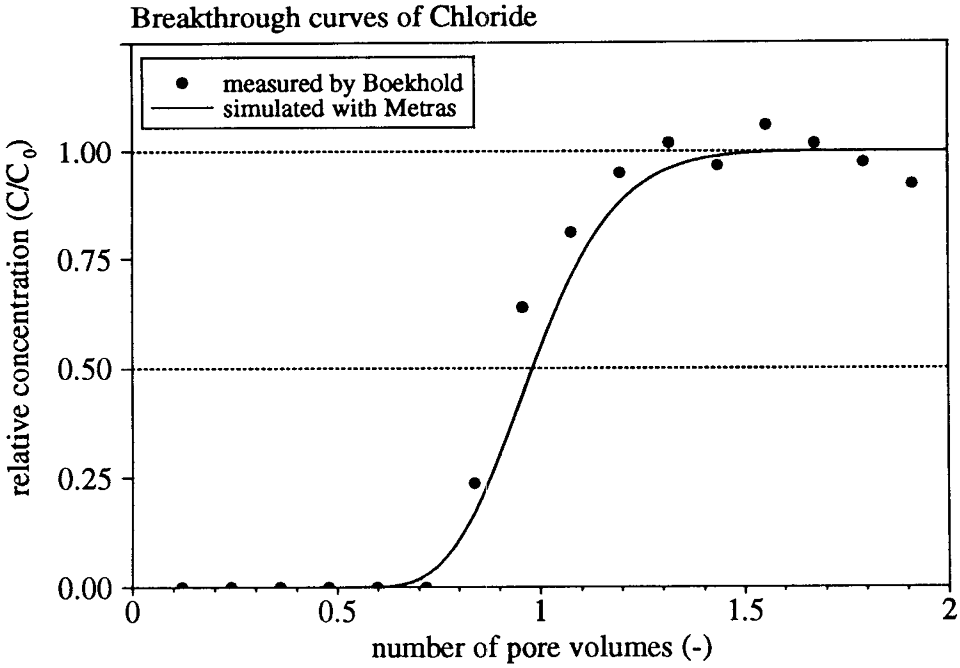

Figure C2 Verification of the obtained dispersion length

APPENDIX D User manual

D.1 Installing and running the model

D.1.1 Platforms and compilers

All SOTRAS models (including METRAS) were written in standard FORTRAN-77, and were tested using the following compilers:

- Salford FTN77/486, version 2.71 (MS-DOS),
- MicroSoft Fortran, version 5.10 (MS-DOS),
- HP FORTRAN/9000, series 700 (UNIX workstation).

For these compilers, standard installation procedures are available. In case of using METRAS on a personal computer, a coprocessor is indispensable. In case of compiling METRAS with other compilers, these compilers must accept the following non-standard FORTRAN-77 extensions:

- Source code in lower case,
- Symbolic names longer than 6 characters,
- Include,
- Implicit none.

Virtually all FORTRAN-77 and all FORTRAN-90 compilers accept these extensions. Under the MS-DOS operating system, it is absolutely necessary to have a good memory manager installed to break through the 640 kByte boundary.

D.1.2 Installation (standard version)

The model (version 2.1) comes on a floppy disc containing the source code of all submodels, a run file, input files and tools. The run file was created with the MicroSoft FORTRAN compiler and can be used directly (no additional files necessary). Compiling the program is necessary when:

- a different compiler is used,
- when METRAS is used on a workstation or
- when the number of soil compartments exceeds 50 or the number of constituents exceeds 10.

The procedure for recompiling the programme is described in Appendix D.1.3.

Directory structure of the METRAS floppy disc

```
\
*------- sotras
         *------- sishell
         *------- sotras
         *------- eqcad
         *------- metras
         *------- bin
         *------- metrinp
         *------- xy
```

The model should be installed using the following commands:

Step 1
Change to the floppy disc, for example drive A:

```
A:
```

Step 2
Copy the contents of the floppy disc to your hard disc. Use the XCOPY command /S switch, to copy subdirectories as well. If another SOTRAS model (for example PESTRAS or SWIF) has already been installed, than common submodels or libraries will be overwritten.

```
XCOPY *.* C:\SOTRAS/s
```

Step 3
Goto the BIN directory:

```
C:
CD \SOTRAS\BIN
```

Step 4
Type `BINZIP` to extract all executables. After extracting, remove the file BINZIP.EXE

Step 5

- Add the directory C:\SOTRAS\BIN to your path

OR --

- Copy the files to a directory which is already in your path).

Step 6
Goto the directory C:\SOTRAS\XY and type `XYZIP` to extract all XY files.

Step 7
You now have two options:

- Add the line `SET XY_DEF=C:\SOTRAS\XY` to the file autoexec.bat

OR --

- Move the contents of the directory C:\SOTRAS\XY to a new directory C:\XY

D.1.3 Installation (non-standard version)

METRAS has been tested and verified under the MS-DOS operating system (Salford FTN77/486 and MicroSoft Fortran, version 5.10), and under the UNIX operating system (HP workstation, series 700). The full procedure for installing the program is as follows:

1 Copy the contents of the floppy disc to your hard disc, using the XCOPY command (see the text frame at page 80). When installing METRAS onto a workstation, be sure that your workstation is mounted before copying - or use a file transfer program (e.g. FTP). Be sure that the directory "sotras" is in the root directory (C:\SOTRAS for MS-DOS or $HOME\SOTRAS for UNIX).

2 The sources are in the subdirectories of \sotras. First decompress the files in all source directories (all source directories contain self-extracting archives). The sources have extension .for. When you want to install METRAS on a UNIX workstation, please perform the following two actions on all of these subdirectories:

- convert all sources to UNIX format. For HP-UX, the command for copying is:

  ```
  ux2dos < dosfile > uxfile
  ```

  For other systems, please check your system manual.
- Alter the extension of the source file into .f:

  ```
  mv source.for source.f
  ```

3 Check the array size in the include file 'sishell.h'. This file will be found in all source directories. Alter the array sizes, when necessary. The three most important array sizes are:

- ml Maximum number of (numerical) soil layers (default = 50)
- mc Maximum number of components (= pesticides; default = 10).
- mhor Maximum number of real soil horizons (i.e. maximum number of retention and conductivity characteristics; default = 5).

Make sure that the include file is copied to all source subdirectories. Otherwise, conflicts may occur between the submodels. IF YOU HAVE ALREADY INSTALLED OTHER SOTRAS MODELS (SWIF, PESTRAS, HEATRAS OR VAPTRAS) INTO THIS DIRECTORY, BE SURE THAT YOU DON'T GET CONFLICTS WITH THESE MODELS. THESE MODELS USE THE SAME INCLUDE FILES!!!!!!

4 When working with the MicroSoft compiler, add the following line to the include file 'sishell.h':

```
$LARGE
```

Without this directive, problems may occur during the link phase.

5 The source subdirectory sishell contains some compiler specific subroutines. These files have extension .msf (MicroSoft), .sal (Salford) and .ux (UNIX), respectively. Copy these files to a file with the same base name, but with extension .for (MS-DOS) or .f (UNIX).

6 All source directories contain 3 make files:

• makemsf	(MicroSoft)
• makesal	(Salford)
• makeux	(UNIX)

Copy these files to the file "makefile" and run the make utility {by typing "nmake" (MS-DOS) or "make" (UNIX)} to compile all sources. End with the subdirectory sotras\metras". The final result is an executable in the subdirectory bin. For other compilers, no makefiles are available. Please alter the existing makefiles or build a new one.

7 Now add this directory to your path (or copy the executable to another directory which is already in your path).

D.2 Running the programme

Once installed properly (§D.1.2), the model is run by typing "metras" followed by the name of the general input file (introduction of §D.3).

Command for running METRAS

Step 1
Create an input file in your favourite ASCII editor (VI, PE, etc.). The simplest way is to edit the example file metras.inp, which is in the directory SOTRAS\METRINP

Step 2
Run the model. Goto the directory C:\SOTRAS\METRINP and type:

```
METRAS.inp
```

Step 3
Create a graph of the major model results by typing:

```
xy -j metras.job -W p
```

Further details on the graphical tool XY are in Van Heerden and Tiktak (1994).

The input file must be created in advance with a normal ASCII editor. Model input is described in detail in §D.3.

D.3 Description of model input

METRAS requires a number of input files, that have to be made in advance. For preparation of the input files, an ASCII editor should be used. Users working in an environment with both UNIX workstations and PC's should not forget to convert the input files to the appropriate (UNIX or MS-DOS) format before starting the programme. The following input files must be prepared:

- a *general input file*, containing control parameters and system parameters. This input file can be broken up in five sections:
    - general control section,
    - soil hydrology and soil temperatures,
    - initial and boundary conditions of the chemical submodel,
    - chemical transport and
    - chemical equilibria.
- a file containing fluxes of major components through the *upper boundary*,
- a file containing *soil pH as a function of time and depth*.

In the description of the input files, strings that must be typed literally are printed in **bold face**. Values are examples only.

D.3.1 The general input file

The general input file consists of **records** and **tables**, each record and table containing the following information (see also the example):

- data,
- identifier (i.e. name of the input parameter),
- (when relevant) the dimension of the input data.

The programme looks for the identifier in the input file, checks the dimension and finally reads the data. The sequence of records and tables is free. All data is read free format (i.e.: it is not necessary to position the data at certain positions within a line).

A **record** can have one of the following forms:

```
integer        identifier      dimension
real           identifier      dimension
option         identifier
```

A **table** has the following general form:

```
table          identifier      dimension
x(1) y1(1)     y2(1)    ..     ym(1)
..
x(n) y1(n)     y2(n)    ..     ym(n)
end_table
```

Here, n refers to the number of data points in the table, and m refers to the number of Y-columns in the table.

Depth dependent soil properties are read from special tables. The user specifies the soil properties for an arbitrary number of depths in the soil, and the program calculates the value at the position of the nodal points by linear **interpolation** or with a **histogram** function. These tables take one of the following two forms (see also Figure D1).

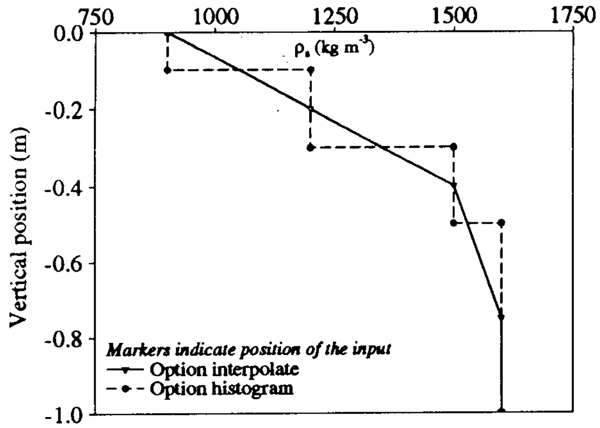

Figure D1 Graph showing the effect of table option interpolate & histogram

```
* An "interpolate" table.
table interpolate identifier dimension
x(1)     y1(1)          ..  ym(1)
..
x(n)     y1(n)          ..  ym(n)
end_table
* A histogram table. The first line is valid for
x(1) up to x(2); x(2) not included!
table histogram identifier dimension
x(1)     x(2)           y1(1)  ..   ym(1)
 ..
x(n-1)   x(n)           y1(n)  ..   ym(n)
end_table
```

Comment can be added to the input files, wherever wanted. However, when comment is positioned on separate lines we recommend to place an asterisk before the actual comment. Comment within tables is illegal! The example below shows part of the general METRAS input file.

```
* Example of a record containing an option:
repeat    ploughtable            Ploughing at same date each year.
* Example of a record containing a real:
0.002     alpha          [m]     Dispersion length
* Example of a depth dependent table (histogram function).
* Bulkdensity as a function of depth.
table     histogram      bulkdensity      [kg*m-3]
0.0  -0.1  1300.0
-0.1 -0.3  1500.0
-0.3 -5.0  1700.0
end_table
```

D.3.2 Control section of the general input file

The general control section of the input file contains the following subsections:

- hydrological submodel selection,
- file control,
- time control,
- discretisation of the soil profile, and
- output control options.

Hydrological submodel selection

The user can make a choice between three options for calculating or reading the hydrological state variables and flux variables:

stationary	The hydrological fluxes and state variables are constant in time (stationary hydrology). The user has to specify a table with hydrological fluxes and soil water contents as a function of vertical position within the soil profile.
simulate	METRAS simulates the hydrological fluxes and soil water contents using the soil water submodel SWIF (on-line coupling). A full description of this submodel and it's parameters is found in Tiktak *et al.* (1994b). This report describes the stationary version only.

Section 1.1: Submodel selection

```
* Controls the hydrological submodel used (make a choice of one of these 2 options):
stat|simulate      watertransport
```

File control

The METRAS input file can be broken up into separate files, if wanted. The same applies to the output files. Opening input- and output files is controlled in lines with the identifier input_ and output_, as shown below:

Section 1.2: File control

```
* When set to "yes" a file is opened for the submodel considered, when set to "no", the
* submodel uses the same file as the shell.
yes|no          input_metras
yes|no          output_metras
```

File names

Apart from the name of the general input file, all file names are read from the general input file. METRAS always asks for a general output file (called 'sishell output file'), for the name of the file with pH values, and for the name of the file with concentrations at the upper boundary. Depending on the hydrological submodel loaded, the programme also asks for the name of the file with meteorological data, conductivity characteristics and retention characteristics. When each submodel should write it's data to separate output files, the program also asks for these names. All file names are to be specified in combination with a label. This label always ends with a colon. A full path can be specified. See the example below:

Section 1.3: File names

```
* METRAS first asks for a general output file.
* sishell output file: $HOME/sotras/metrinp/metras.inp

* METRAS always asks for the following two files (concentration at the
* upper boundary and pH as a function of time and depth):
* concentration ub: $HOME/sotras/metrinp/metras.bnd
* ph profiles: metras.ph

* When using SWIF, METRAS also asks for these three file names:
* meteorology: $HOME/sotras/metrinp/debilt.dat
* conductivity characteristics: $HOME/sotras/swifinp/kh.001
* retention characteristics: $HOME/sotras/swifinp/pf.001

* When the user wants to use separate files for each submodel, add the following lines (in this
* example separate files were opened for the submodel SWIF):
* swif input file: $HOME/sotras/swifinp/swif.001
* swif output file: $HOME/sotras/swifinp/swif.out
```

Time control

In the general control section of METRAS, the time of start of the simulation (tstart), the end time (tend) and the print interval must be specified (prstep). It is also possible to suppress screen output during execution of the dynamic part of the simulations (print_time). Moreover, the maximum time-step can be set explicitly. However, under normal

Section 1.4: time control

```
* Start and end time of the simulations. In this example 0 and 3650, respectively.
0.0       tstart        [d]
3650.0    tend          [d]

* Print interval. In this example set to 5.
5.0       prstep        [d]

* Maximum time-step in the chemical transport submodel.
1.0       dtmaxsotras   [d]

* Control screen output. If set to "no", screen output is suppressed.
yes|no    print_time
```

Discretisation and horizon stratification

In this section, the vertical position of the boundaries of the numerical compartments must be specified. For each compartment, the user must also specify the horizon number. When using the hydrological submodel SWIF, the numbers of the retention and conductivity characteristics must also be specified.

When the user has decided to use separate input files for each submodel (page 85), the corresponding discretisation table must be included in each input file (e.g. swif discretisation in the SWIF specific input file).

Section 1.5: Discretisation and horizon stratification

```
* Discretisation and numbers of the retention and conductivity characteristics to be used.
* For each submodel, separate tables can be supplied, but it is also legal to combine the
* tables into one table. In this example, the reference height is set to zero.
0.0        zref           [m]
* The table is valid for all submodels included in the list preceding the word discretisation.
* Column 1 contains the vertical position, column 2 the horizon number, column 3 the number
* for the retention characteristic and column 4 the number for the conductivity characteristic.
shell, swif, and metras    discretisation          [m]
-0.1  1    1     1
-0.2  1    1     1
..
-4.5  1    2     3
-5.0  1    2     3
end_table
```

Output control

Model output is flexible. For each parameter in the output list, a print flag must be set which indicates whether this variable must be printed or not. For all variables that are depth dependent, the nodes that must be output can also be specified. The output variables are described in §D.4.

Section 1.6: Output control

```
* For each output parameter, a print flag must be set. This flag may be set to yes or no.
* The name of the print flag is the name of the output parameter preceded by 'print_'.
* In the example below, the name of the output variable is 'cmob'. The output variables are
* specified in §D.4.
yes|no          print_cmob      Print variable cmob if set to yes

* For depth dependent variables, the nodes that are to be output must be specified. This list
* must be specified for each submodel, but they may be combined. In the example below,
* nodes 1, 5 and 10 are output for all submodels:
metras, swif, heattras and shell print_rows
1
5
10
end_list

* If the substring 'all' is added, all nodes are output:
metras, swif, heattras and shell print_rows all
```

D.3.3 Soil hydrology and soil temperatures

Stationary soil water and heat transport

When option 'watertransport' is set to 'stationary', soil water contents, soil water pressure heads, soil water fluxes and soil temperatures must be supplied by the user. In this case, the hydrological submodel SWIF is not loaded.

Variable name	identifier	dimension
• Root water uptake flux	vwat	($m\ d^{-1}$)
• Volumetric water content	theta	($m^3\ m^{-3}$)
• Soil water pressure head	preshead	(m)
• Soil temperature	temp	(°C)

Non-stationary soil water transport

When option 'watertransport' is set to 'simulate', the submodels SBOUND, SWIF and HEATRAS are loaded. A full description of the input parameters for these submodels can be found in Tiktak *et al.* (1994b), page 43-51.

Section 2.: Stationary soil hydrology

```
* The following properties are depth dependent and must be specified in a histogram or
* interpolate table
table     interpolate   vwat        [m*d-1]
0.0  -0.01                                  Column 1: Vertical position
-5.0 -0.01                                  Column 2: Vertical soil water flux
end_table

table     interpolate   theta       [m3*m-3]
0.0  0.25                                   Column 1: Vertical position
-5.0 0.25                                   Column 2: Soil water content
end_table

table     interpolate   preshead    [m]
0.0  -0.1                                   Column 1: Vertical position
-5.0 -0.1                                   Column 2: Soil water pressure head
end_table

table     interpolate   temp        [oC]
0.0  9.97                                   Column 1: Vertical position
-5.0 9.97                                   Column 2: Soil temperature
end_table
```

D.3.4 Initial and boundary conditions of the chemical submodel

Initial contents

The initial condition of METRAS (viz. initial content of each component) is input through a table. Both 'interpolate' and 'histogram' tables are valid.

Upper boundary condition

The concentration of all components at the upper boundary (i.e. the concentration of components in water infiltrating into the soil) must be input through a separate file, the name of this file must be specified in the general input file.

Partial CO_2 pressure, pH, and ionic strength.

The concentration of CO_2 must be input to the model. It can be calculated with an external model (for example the VAPTRAS model (Freijer *et al.*, 1995). The same applies for the file with pH values as a function of time and depth. pH is an important boundary condition for the model, which can be simulated with one of the models ReSAM (time-step 1 year) or NuCSAM (timestep one day). This file consists of columns, containing the pH value for a given number (**nph**) of soil layers. The depth of these soil layers must be specified in the general input file (see below). The ionic strength of the soil solution is another boundary condition for the model.

Section 3.: Initial and boundary conditions of the chemical submodel

```
* Initial content (mol m-3) of each component.
* Column 1 & 2:      depth
* Column 2:          Initial content of Cd (= Cd2+ + CdCl2 + CdSO4 + CdCO3)
* Column 3:          Initial content of Cl (= Cl- + CdCl)
* Column 4:          Initial content of SO4 (= SO42- + CdSO4)
* Column 5:          Initial content of CO3 (= CO32- + CdCO3)
table    histogram   conc_ini      [mol*m-3]
0.095 -4.5           0.0     0.0     0.0     0.0
end_table

* Name of the file with the concentration at the upper boundary:
* concentration ub: metras.bnd

* Name of the file with pH values:
* ph profiles: metras.ph
6    nph [-]    Number of columns in the file with pH values
* The following line contains the boundaries for the above mentioned columns.
* This line must contain one more value than the number specified above.
0.095    -0.025 -0.125  -0.225  -0.425  -0.625  -4.000  pHz    [m]

* CO2 pressure is also considered a boundary conditions for the model:
table    interpolate    cco2g   [bar]
0.095    0.0003
-4.5 0.03
end_table

* Ionic strength as a function of depth:
table    interpolate    strion   [mol*L-1]
0.095    0.005
-4.5 0.005
end_table
```

Variable name		identifier	dimension
• initial content of each component	c	conc_ini	(mol m^{-3})
• ionic strength	I	strion	(mol L^{-1})
• pH	pH	pH	(-)
• partial CO_2 pressure	pCO_2	cco2g	(bar)

D.3.5 Soil chemical transport

METRAS needs the dispersion length, the molecular diffusion coefficient of each component in water and the tortuosity. The tortuosity is a function of water content and must be supplied as a table.

Variable name		identifier	dimension
• Dispersion length	L_{dis}	alpha	(m)
• Molecular diffusion coefficient in water	D_o	d0	(m^2 d^{-1})
• Tortuosity	λ	lambda	(-)

Section 4.: Chemical transport parameters

```
* The dispersion length is dependent on soil properties only. The molecular
* diffusion coefficient in water is component dependent. The tortuosity factor is dependent
* on soil properties and soil water content.
0.051          alpha         [m]           Dispersion length.
0.4E-4         d0_cd         [m2*d-1]      Diffusion coefficient in water.
0.4E-4         d0_so4        [m2*d-1]

table    lambda        [-]
0.000    0.000                   Tortuosity as a function of the water content.
0.035    2.0E-4                  1st column: water content (m3 m-3).
..                               2nd column: tortuosity (-)
..       ..                      Values in between are obtained by linear
0.600    0.600                   interpolation.
end_table
```

D.3.6 Equilibria

The cadmium implementation of METRAS, METRAS-CD, needs the soil organic carbon content, the dry bulk density of the soil, and parameters of the extended Freundlich equation.

Variable name		identifier	dimension
• Organic carbon content	*oc*	ctcarbon	(%)
• bulk density of dry soil	${}^{b}\rho_{s}$	bulkdensity	(kg m^{-3})
• Scaled sorption Freundlich coefficient	K^{*}	kstar	(mg^{1-n} kg^{-1} L^{n})
• exponent in Cd^{2+} part of Freundlich eq.	n	freundn	(-)
• exponent in H^{+} part of Freundlich eq.	m	freundm	(-)

Section 5.: Parameters for the equilibrium submodel

```
* Organic carbon content as a function of depth
table     histogram      ctcarbon        [-]
0.095      0.060 0.03485
0.060      0.000 0.03274
0.000     -0.025 0.02538
end_table

* Dry bulk density as a function of depth
table     histogram      bulkdensity     [kg*m-3]
0.095     0.000  110.0
0.000     -0.025 1300.0
-0.025    -4.5   1700.0
end_table

* Parameters for the extended Freundlich equation
table     histogram      freund_cd       [mg*kg-1]
0.095     -4.500 0.051   0.69    -0.5
end_table

* Parameter controlling the equilibrium solver
0.1       acrelnr        [-]             Relative accuracy Newton Raphson procedure
1.d-18    acabsnr        [mol*L-1]       Absolute accuracy Newton Raphson procedure
1.d-14    acmin          [mol*L-1]       Minimum [Cd2+] for equilibrium calculation
1.d-17    acsat          [mol*L-1]       Absolute accuracy precipitation calculation
```

D.3.7 Upper boundary condition

METRAS needs the concentration of each component in the solution that infiltrates into the soil. These concentrations should be specified in a separate input file, which name must be specified in the general input file (see §D.3.2):

General input file: concentration at the upper boundary

```
* The name of the file with concentration at the upper boundary must be specified
* in the general input file
* concentration ub: metras.bnd
```

The file with concentrations at the upper boundary has the following format (figures are examples from the Kempen case):

The file with concentrations at the upper boundary

```
* Boundary conditions for the Kempen case
* Comment lines must start with an asterisk. They may not be placed after the first data line.
* Column 1: Start time of period for which data are valid.
* Column 2: End time of period for which data are valid.
* Column 3: Concentration of Cd components in infiltrating water (mol m-3)
* Column 4: Concentration of Cl components in infiltrating water (mol m-3)
* Column 5: Concentration of SO4 components in infilt rating water (mol m-3)
*
* tstart        tend          Cd           Cl            SO4
* (d)           (d)           -----        (mol m-3)     -------
1.0      6936.0               3.430E-06    0.173         0.148
6936.0          7301.0        4.717E-06    0.173         0.148
                              etc.
```

D.3.8 pH as a function of time and depth

METRAS needs pH values as a function of time and depth. pH values must be specified in a separate input file, which name must be specified in the general input file (see §D.3.2).:

General input file: pH as a function of time and depth

```
* The name of the file with pH profiles must be specified in the general input file.
* METRAS also needs information about the format of the pH file.
* ph profiles: metras.ph
6   nph [-]    Number of columns in the file with pH values
* Height of the boundaries for each column. Number of figures must be one higher than nph.
0.095    -0.025 -0.125  -0.225  -0.425  -0.625  -4.500          pHz    [m]
```

The file with pH values has the following format (in this example, the number of columns (nph) is 6.

The file with pH profiles

```
* pH profiles for the Kempen case.
* Comment lines must start with an asterisk. They may not be placed after the first data line.
* Column 1:          Start time of period for which data are valid.
* Column 2:          End time of period for which data are valid.
* Column 3-8:        pH for each layer. Depths are specified in the general input file.
*
* The start time for each time-interval must be equal to the end-time of the preceding
* interval. If option 'equalyears' is set to 'repeat', the first date must be 1.0 and the last
* date must be 365.0
*
* tstart       tend             pH       pH       pH       pH       pH       pH
* (d)          (d)              layer 1  layer 2  layer 3  layer 4  layer 5  layer 6
1.0      365.0          4.00    5.00     5.00     5.00     5.00     5.00
365.0          730.0            4.00     4.97     4.98     4.98     4.98     4.98
                                etc.
```

D.4 Description of model output

D.4.1 Output control

Model output is flexible. For each parameter in the output list, a print flag may be set which indicates whether this variable must be printed or not. This print flag must be specified in the general METRAS input file (see §D.3.2). For all variables that are depth dependent, the nodes that must be output have to be specified. All output variables are described in this chapter.

Depending on the actual value of options **output_metras**, all output is written to one big output file or written to two (smaller) files (see §D.3.2).

D.4.2 Output format

The output of METRAS consists of records. Each records contains the following information:

```
time   identifier      data(1)     ..     data(n)
```

where n is the number of elements to be output. The output is written according to the following FORTRAN format:

```
format (f9.3,1x,a12,1x,50(g12.4,:))
```

Output control

```
* For each output parameter, a print flag must be set. This flag may be set to yes or no.
* The name of the print flag is the name of the output parameter preceded by 'print_'.
* In the example below, the name of the output variable is 'theta'. The output variables are
* specified in §D.4.
yes|no          print_theta        Print variable theta if set to yes

* For depth dependent variables, the nodes that are to be output must be specified. This list
* must be specified for each submodel, but may be combined. In the example below, nodes 1,
* 5 and 10 are output for all submodels:
metras and hell print_rows
1
5
10
end_list

* If the substring 'all' is added, all nodes are output:
metras and shell print_rows all
```

See the following example:

```
2931.000 theta      .2881         .3131         .3298
```

The first time, METRAS also prints the dimension of the output, e.g.:

```
2930.000 theta      .2850         .3107         .3278        [m3*m-3]
```

The output can be processed with the spreadsheet interface programma SR (§D.4.3) and plotted with the graphical tool XY (§D.4.3).

D.4.3 Output processors

The spreadsheet interface SR

With SR (Select Records), lines can be chosen from the output according to user specified criteria. These lines can be imported in a spreadsheet, such as Lotus 123. SR is called from the DOS or UNIX prompt as follows:

```
sr ColumnNumber identifier < METRASOutputfile > SelectionFile.
```

Here, identifier is the string to be searched for and ColumnNumber refers to the column with the identifier (in the METRAS outputfile column 2). See the following example, in which all lines with the string theta in the 2nd column are selected:

```
sr 2 theta < metras.out > theta.out
```

The graphical tool XY

METRAS output can be plotted without any data conversion with the graphical tool XY. A full description of this programme is given in Van Heerden and Tiktak (1994). Here, a brief description of XY is given.

XY reads all plot settings from an ASCII file. First, you have to specify the data series to be plotted. This must be done with the DATA command, which has the following general format:

```
DATA FileName   Column_X   Column_Y   Column_Identifier   Identifier
```

Here, FileName is the name of the METRAS output file, Column_X is the column number containing the graph series X points (usually the time, in METRAS outputfile column 1), Column_Y is the column number with the graph series Y points and Column_Identifier is the column number with the identifier (in METRAS output column 2). Consider the following example, in which theta of node 1 is plotted as a function of time (the format of the output is shown on page 95):

```
DATA metras.out 1 3 2 theta
```

A maximum of up to 9 data series can be plotted with XY. The data series can be in different files, as in the following example:

```
DATA metras.out 1 3 2 theta
DATA theta.dat 1 2
```

The graph settings can be adopted with separate commands. With the X_AXIS and Y_AXIS commands, the axis settings can be changed. With the X_TEXT en Y_TEXT commands, text can be plotted along the axis. With the LEGEND command a legend is plotted and a maximum of two titles can be plotted with the TITLE_1 and TITLE_2 commands. See the following example:

An XY configuration file

```
* Selection of data series:
data metras.out 1 3 2 theta
data theta.dat 1 2
* Legend of the data series (string must start and end with a quote):
legend 'Simulation results' 'Measurements'
* Axes settings. X minimum is 0, maximum is 0.4. Y minimum is 0 and maximum 0.4.
* Number of tics along X axis is 12 and along the Y axis 4:
x_axis 0 360 12
y_axis 0 0.4 4
* Text along the axes:
x_text Day number (1989)
y_text Water content (m3/m3)
* Titles:
title_1 Water content as a function of time
title_2 (Run 027a)
```

XY must be called from the DOS or UNIX prompt as follows:

```
xy -c configuration file
```

D.4.4 Model outputs

Depth dependent variables output by the submodel METRAS are averages over the METRAS grid (specified in the **table metras discretisation**; page 87, 88). The number of nodes to be output are controlled by **table metras print_rows** (page 87, 88). Fluxes are also averages over one print interval (controlled by **prstep**; page 86). Some model outputs refer to components, while others refer to species (see definitions). In the table below, this is indicated in the column 'comp.'.

The following variables are output:

Variable name	size	comp.	identifier	dimension
• Average time step in METRAS	1	-	dtmetras	(d)
• Number of iterations in equilibrium solver	1	-	isteps	(-)
• Mass balance error in equilibrium solver	1	-	trblnc	(mol m^{-2})
• Total areic mass	mc	YES	tma	(mol m^{-2})
• Areic mass in liquid phase	mc	YES	tmal	(mol m^{-2})
• Areic mass sorbed	mc	YES	tmaso	(mol m^{-2})
• Areic mass balance error	mc	YES	tmaerr	(mol m^{-2})
• Flux through upper boundary	mc	YES	vub	(mol m^{-2} d^{-1})
• Cumulative flux through upper bound.	mc	YES	tvub	(mol m^{-2})
• Content of each component in the soil system	ml.mc	YES	ctot	(mol m^{-3})

• Concentration of each component in the liquid phase	ml.mc	YES	cmob	(mol m^{-3})
• Content of each species sorbed onto the soil solid phas	ml.mc	NO	cabs	(mol m^{-3})
• Concentration of each species in the liquid phase	ml.mc	NO	cliq	(mol m^{-3})
• Content of precipitates	ml.mc	NO	cprc	(mol m^{-3})
• Mass flux of each component	ml.mc	YES	vsub	(mol m^{-2} d^{-1})
• Convective mass flux of component	ml.mc	YES	vcon	(mol m^{-2} d^{-1})
• Dispersive mass flux of component	ml.mc	YES	vdis	(mol m^{-2} d^{-1})
• Cumulative mass flux of component	ml.mc	YES	tvsub	(mol m^{-2})
• Total areic mass content from $z=z_{ref}$ to z	ml.mc	YES	actot	(mol m^{-2})
• Total areic mass content in the liquid phase from $z=z_{ref}$ to z	ml.mc	YES	acmob	(mol m^{-2})